REGISTERED No. M. 3121

UNIVERSITY OF MICHIGAN
SEP 19 1955
PHYSICS LIBRARY

PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. XLII] *SECTION A* [No. 1

JULY 1955

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

THE ELASTIC BEHAVIOUR OF ISOTROPIC SOLIDS

By Sir C. V. Raman and K. S. Viswanathan
(*Memoir No. 72 of the Raman Research Institute, Bangalore 6*)

Received July 8, 1955

1. Introduction

It is a classic result in the phenomenological theory of elasticity that *two* independent constants suffice to describe the stress-strain relationships for an isotropic solid. If, for example, the bulk modulus and the shear modulus of the material are known, Young's modulus and Poisson's ratio may be calculated therefrom. In the present paper, the ideas regarding the nature of the strains and stresses in solids on which the derivation of this result is based are critically examined and it is shown that they are untenable. A re-formulation of the phenomenological theory of elasticity not open to the same objections is then presented and its consequences are developed. It emerges that *three* independent constants are needed to describe the stress-strain relationships of an isotropic body; in particular, it is shown that the bulk modulus of the material cannot be evaluated from the experimental data for the velocities of propagation of longitudinal and transverse waves respectively in the solid and its density.

2. Some General Considerations

As is well known, the elastic constants of solids can be determined independently by static and dynamic methods. The latter are based on measurements of the velocity of propagation of waves of different types in the material. In all studies of this nature we are clearly concerned with *heterogeneous* strains, in other words with strains which are not of the same magnitude throughout the solid at any given instant; clearly, there could be no wave-propagation if the strains were the same everywhere. On the other hand, in the static methods of measuring elastic constants the strains may be homogeneous or heterogeneous according to the nature of the experiment. The change in volume of a solid under hydrostatic pressure is a case of the first kind, while the twisting of a rod by couples applied at its two ends is clearly a case of heterogeneous strain. The examples cited are sufficient to show that any theory of elastic behaviour has necessarily to concern itself with *heterogeneous* strains; a theory which restricts itself to the consideration of homogeneous strains would be fundamentally incomplete.

The twisting of a rod by couples applied at its two ends also serves to illustrate certain fundamental aspects of the theory of elasticity. As just mentioned, it is an example of heterogeneous strain, and indicates that the movements of the parts of the solid in such strains may be angular movements or rotations, the magnitude of which varies through the volume of the solid. Thus, we are forced to recognize that the strains in a solid cannot, in general, be described solely as *elongations* but may also include *twists*. Further, in the case referred to, the external stresses applied to the body are *couples*. It follows that the internal stresses may also be of the same nature. In other words, the stresses in an elastic solid cannot be assumed to be exclusively in the nature of *tractive forces* but may also include *torques*.

The arguments in the classical theory of elasticity by which the familiar result quoted in the opening sentence of the paper are derived may be summed up briefly as follows: that it is sufficient to consider the case of homogeneous strains; that any homogeneous strain may be analysed into a " pure strain " and a rotation and that the latter should be ignored in formulating the stress-strain relationships; and finally that the tractive forces assumed to act on elements of area in the solid are so related that no torques tending to rotate the volume-elements of the solid are present. Everyone of these statements is at variance with the considerations set forth above. It follows that the argument with all its consequences is unacceptable.

3. FORMULATION OF THE THEORY

If now we denote by u_x, u_y, u_z the three components of the displacements of a point (x, y, z) of the material and by $u_x + u_x'$, $u_y + u_y'$, $u_z + u_z'$ the corresponding displacements of a neighbouring point situated at $(x + x', y + y', z + z')$, then it is a well-known result that the strains in the neighbourhood of the point (x, y, z) can be represented by the scheme of equations

$$\begin{aligned} u_x' &= u_{xx}x' + u_{xy}y' + u_{xz}z' \\ u_y' &= u_{yx}x' + u_{yy}y' + u_{yz}z' \\ u_z' &= u_{zx}x' + u_{zy}y' + u_{zz}z' \end{aligned} \qquad (1)$$

where u_{xy} stands, for brevity, for the differential coefficient $\frac{\partial u_x}{\partial y}$.

In view of what has been said in the previous section, all the nine components of strain figuring in the equations (1) are required for a complete specification of the deformations in which rotations are not ignored. Then the changes in the state of a volume element contemplated in (1) can be

analysed into (i) changes of volume, (ii) changes in shape not involving rotations or alterations of volume, and (iii) rotations.

Likewise, the stresses in the interior of the solid require nine components for their full specification. Denoting by $T_{x\nu}$, $T_{y\nu}$ and $T_{z\nu}$ the components of the tractive forces parallel to the three axes of co-ordinates on any elementary area whose normal has a specified direction ν, these tractions are related to the stresses acting on the three co-ordinate planes by means of the relations

$$\begin{aligned} T_{x\nu} &= T_{xx}\cos(x,\nu) + T_{xy}\cos(y,\nu) + T_{xz}\cos(z,\nu) \\ T_{y\nu} &= T_{yx}\cos(x,\nu) + T_{yy}\cos(y,\nu) + T_{yz}\cos(z,\nu) \\ T_{z\nu} &= T_{zx}\cos(x,\nu) + T_{zy}\cos(y,\nu) + T_{zz}\cos(z,\nu) \end{aligned} \tag{2}$$

As mentioned earlier, the three components of the angular momenta of any volume element will not vanish in dynamic experiments or for heterogeneous strains involving rotations and which accordingly involve torques. We therefore retain all the nine stress components in our formulation and do not make the usual reduction in their number from nine to six.

At this stage, we introduce a slight change in notation which enables us to pass on from symbols with double subscripts to symbols involving a single suffix only. We use for the stress components

T_{xx} T_{yy} T_{zz} T_{yz} T_{zy} T_{zx} T_{xz} T_{xy} T_{yx} the symbols

T_1 T_2 T_3 T_4 T_5 T_6 T_7 T_8 T_9 respectively and similarly write the strain variables

u_{xx} u_{yy} u_{zz} u_{yz} u_{zy} u_{zx} u_{xz} u_{xy} u_{yx} as

u_1 u_2 u_3 u_4 u_5 u_6 u_7 u_8 u_9 respectively.

With this notation the stress-strain relations take a neat form. Since the stresses in the solid are dependent on the strain produced in the solid, the stress components can be expanded as a power series in the strain variables. If we measure the stresses from an initial state corresponding to the undeformed condition of the solid and consider infinitesimal strains only, so that squares and higher powers of the strain variables can be neglected in comparison with first order terms, the stresses at any point of the solid are linear functions of the strain components at that point. The stress-strain relations can then be expressed as

$$T_m = \sum_{n=1}^{9} d_{mn}\, u_n \quad (m = 1, 2 \ldots 9) \tag{3}$$

and these involve 81 constants. Here the constant d_{mn} relates the stress T_m to the strain u_n and is the ratio of the two for a deformation in which all strain components other than u_n vanish.

The 81 constants figuring in (3) are not all independent, but reduce in the first instance to forty-five for all solids in view of the relations

$$d_{mn} = d_{nm} \ (m, n = 1, 2 \ldots .9) \tag{4}$$

These relations follow from the well-known theorem of reciprocity relating forces and the corresponding displacements in dynamical systems.[4] The reciprocity relations further enable us to write down the expression for the deformation energy per unit volume in the neighbourhood of any point and this is given by

$$U = \tfrac{1}{2} \sum_{m=1}^{9} T_m \, u_m$$

or

$$2U = \sum_{m} \sum_{n} d_{mn} \, u_m \, u_n \tag{5}$$

4. THE THREE ELASTIC CONSTANTS OF ISOTROPIC SOLIDS

The isotropic nature of a body results in a great reduction of the number of independent constants occurring in the stress-strain relationships. Most of these constants in fact are zero and the others become equal to each other in sets for isotropic materials. Some of these relations can be deduced easily from simple symmetry considerations, without going into the full details of the analytic apparatus needed to derive them. For example, the cubic symmetry possessed by the material endows it with the same property for all the three directions of the axes of co-ordinates and therefore the stress-relationships should remain invariant under any permutation of the symbols x, y, z in both the strain variables (u_{xy}) as well as in the stress components T_{xy}. We thus get

$$\begin{aligned} d_{11} &= d_{22} = d_{33}; \\ d_{12} &= d_{23} = d_{31}; \\ d_{45} &= d_{67} = d_{89}; \\ d_{44} &= d_{55} = d_{66} = d_{77} = d_{88} = d_{99} \end{aligned} \tag{6}$$

Again, the operations of reflection about any plane in space do not produce observable changes in the properties of isotropic bodies. In the simple case of a reflection about the xy plane, the z co-ordinate of any point changes its sign while its x and y co-ordinates are unaffected. Hence all the strain components like u_{yz} (u_4), u_{zy} (u_5), u_{zx} (u_6), u_{xz} (u_7) in which z

occurs *once* only as a suffix change their sign whereas the other strain variables are unaltered. If therefore we substitute these new values of the strain variables in the energy expression and equate it to the original one, we get

$$d_{14} = d_{15} = d_{16} = d_{17} = d_{24} = d_{25} = d_{26} = d_{27} = d_{34} = d_{35} = d_{36} = d_{37} = d_{48} = d_{49} = d_{58} = d_{59} = d_{68} = d_{69} = d_{78} = d_{79} = 0 \tag{7}$$

Similarly by considering reflections about the planes $x = 0$, and $y = 0$, we could show that

$$d_{18} = d_{19} = d_{28} = d_{29} = d_{38} = d_{39} = d_{46} = d_{47} = d_{56} = d_{57} = 0 \tag{8}$$

Simple symmetry considerations thus reduce the number of non-zero and independent constants to four. Even these constants (*i.e.*) d_{11}, d_{12}, d_{44} and d_{45} however are not independent but are connected to each other by means of a linear relation. To obtain this, we use the special symmetry property possessed by isotropic solids alone, namely invariance in behaviour under all rotations in space. Considering a rotation about the z-axis through an angle θ, this operation changes the strain variables into a new set of quantities $u_1', u_2', \ldots u_9'$ related to the original ones in accordance with the following scheme:

$$\begin{aligned}
u_1' &= u_1 \cos^2\theta + (u_8 + u_9) \sin\theta \cos\theta + u_2 \sin^2\theta; \\
u_2' &= u_1 \sin^2\theta - (u_8 + u_9) \sin\theta \cos\theta + u_2 \cos^2\theta; \\
u_3' &= u_3; \\
u_4' &= u_4 \cos\theta - u_7 \sin\theta; \\
u_5' &= u_5 \cos\theta - u_6 \sin\theta; \\
u_6' &= u_5 \sin\theta + u_6 \cos\theta; \\
u_7' &= u_4 \sin\theta + u_7 \cos\theta; \\
u_8' &= (u_2 - u_1) \sin\theta \cos\theta + (u_8 \cos^2\theta - u_9 \sin^2\theta); \\
u_9' &= (u_2 - u_1) \sin\theta \cos\theta + (u_9 \cos^2\theta - u_8 \sin^2\theta).
\end{aligned} \tag{9}$$

Hence under the operation of a rotation about the z-axis by an amount θ, the energy expression (5) changes into

$$\begin{aligned}
2U = {} & d_{11} u_3^2 + d_{11} \{u_1 \cos^2\theta + (u_8 + u_9) \sin\theta \cos\theta + u_2 \sin^2\theta\}^2 \\
& + d_{11} \{u_1 \sin^2\theta - (u_8 + u_9) \sin\theta \cos\theta + u_2 \cos^2\theta\}^2 \\
& + 2d_{12} (u_1 + u_2) u_3
\end{aligned}$$

$$
\begin{aligned}
&+ 2d_{12}\{u_1\cos^2\theta + (u_8+u_9)\sin\theta\cos\theta + u_2\sin^2\theta\}\\
&\qquad\times\{u_1\sin^2\theta - (u_8+u_9)\sin\theta\cos\theta + u_2\cos^2\theta\}\\
&+ d_{44}\{(u_2-u_1)\sin\theta\cos\theta + u_8\cos^2\theta - u_9\sin^2\theta\}^2\\
&+ d_{44}\{(u_2-u_1)\sin\theta\cos\theta + u_9\cos^2\theta - u_8\sin^2\theta\}^2\\
&+ d_{44}(u_4^2+u_5^2+u_6^2+u_7^2) + 2d_{45}(u_4u_5+u_6u_7)\\
&+ 2d_{45}\{(u_2-u_1)\sin\theta\cos\theta + u_8\cos^2\theta - u_9\sin^2\theta\}\\
&\qquad\times\{(u_2-u_1)\sin\theta\cos\theta + u_9\cos^2\theta - u_8\sin^2\theta\} \qquad (10)
\end{aligned}
$$

Comparing this with the expression

$$
\begin{aligned}
2U = {} & d_{11}(u_1^2+u_2^2+u_3^2) + 2d_{12}(u_2u_3+u_3u_1+u_1u_2)\\
& + d_{44}(u_4^2+u_5^2+u_6^2+u_7^2+u_8^2+u_9^2)\\
& + 2d_{45}(u_4u_5+u_6u_7+u_8u_9) \qquad (11)
\end{aligned}
$$

we get

$$d_{11} = d_{12} + d_{44} + d_{45} \qquad (12)$$

Rotations about the x- and y-axes through any angle should also necessarily lead to the same equation (12). A general rotation about any axis can be effected by a superposition of rotations through different angles about the x, y and z axes. We have thus exhausted all the symmetry operations permissible for isotropic solids. It follows therefore that *the elastic behaviour of isotropic solids requires three independent constants for its description, which may be denoted by* d_{11}, d_{12} *and* d_{44}.

5. Relations between the Various Constants

With the aid of the relations (6), (7), (8) and (12), the stress-strain relationships described by (12) can be rewritten. The expressions for the three stretches T_1, T_2 and T_3 become

$$
\begin{aligned}
T_1 &= d_{11}u_1 + d_{12}(u_2+u_3)\\
T_2 &= d_{11}u_2 + d_{12}(u_3+u_1) \qquad (13)\\
T_3 &= d_{11}u_3 + d_{12}(u_1+u_2)
\end{aligned}
$$

whereas the shearing stresses are given by

$$
\begin{aligned}
T_4 &= d_{44}u_4 + (d_{11}-d_{12}-d_{44})u_5\\
T_5 &= d_{44}u_5 + (d_{11}-d_{12}-d_{44})u_4 \qquad (14)
\end{aligned}
$$

and four similar equations.

We shall now evaluate some of the important elastic constants, *viz.*, the compressibility or bulk modulus, Young's modulus and Poisson's ratio

in terms of these new constants. Consider first the case of a uniform hydrostatic pressure acting at all points on the surface of the body. The state of stress produced by such a compression of the solid is described by $T_1 = T_2 = T_3 = -p$; $T_4 = T_5 = \ldots = T_9 = 0$. Hence adding all the three equations in (13), we get

$$p = \tfrac{1}{3}(d_{11} + 2d_{12})\Delta \tag{15}$$

where Δ denotes the cubical compression $-(u_1 + u_2 + u_3)$. The bulk modulus therefore is given by

$$k = \tfrac{1}{3}(d_{11} + 2d_{12}) \tag{16}$$

Similarly by considering the case of an isotropic body in the form of a cylindrical rod subjected to a tension T which is uniform over its plane ends, we could show that the Young's modulus E and Poisson's ratio σ are related to d_{11} and d_{12} in accordance with the equations

$$\mathrm{E} = \frac{(d_{11} + 2d_{12})\,(d_{11} - d_{12})}{(d_{11} + d_{12})} \tag{17}$$

$$\sigma = \frac{d_{12}}{(d_{11} + d_{12})} \tag{18}$$

These expressions are in the same form as the corresponding ones for k, E and σ of the classical theory expressed in terms of the well-known constants c_{11} and c_{12}. The relations among the Young's modulus, bulk modulus, and Poisson's ratio are therefore the same both in the two-constant as well as in the three-constant theories. We emphasize the fact that all the three equations (16), (17) and (18) contain the constants d_{11} and d_{12} only, and none of them involves d_{44} explicitly. This is because all these modulii are determinable from static homogeneous strains alone, whereas d_{44}, being a constant involving rotations of the volume elements requires experiments involving twists for its evaluation.

It may be pointed out here that the relation (12) may be derived directly from very simple considerations. A cube which is subject to normal tractions on a pair of opposing faces and normal pressures of equal magnitude on an adjacent pair of faces would suffer no change of volume, but would expand and contract respectively in the direction of the two normals to the faces by an amount of which $(d_{11} - d_{12})$ is a measure. Likewise, if a pair of opposing faces of a cube are subject to tangential tractions forming a couple and an adjacent pair also subject to tangential tractions which form a balancing couple, the cube would suffer no change of volume but would undergo a change of shape without rotation of which $(d_{44} + d_{45})$ is readily

seen to be a measure. The two systems of stresses and the resulting strains can readily be shown to be equivalent and it follows that $(d_{11} - d_{12}) = (d_{44} + d_{45})$.

6. VELOCITY OF PROPAGATION OF WAVES IN THE SOLID

In the absence of body forces, the general equations of motion of an elastic body are given by

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} ;$$

$$\rho \frac{\partial^2 u_y}{\partial t^2} = \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z}$$

$$\rho \frac{\partial^2 u_z}{\partial t^2} = \frac{\partial T_{zx}}{\partial x} + \frac{\partial T_{zy}}{\partial y} + \frac{\partial T_{zz}}{\partial z} \qquad (19)$$

where ρ is the density of the material. For an isotropic solid, the stress-strain relations are given by equations (13) and (14). Adopting once again the primitive notation of writing differential coefficients $\partial u_x/\partial x, \ldots . \partial u_y/\partial z \ldots .$ for the strain components $u_1, \ldots . u_4 \ldots .$ etc., we get on substituting (13) and (14) in (19) that

$$\rho \frac{\partial^2 u_x}{dt^2} = (d_{11} - d_{12}) \nabla^2 u_x + d_{12} \frac{\partial \Delta}{\partial x}$$

$$+ (d_{11} - d_{12} - d_{44}) \left\{ \frac{\partial}{\partial z}\left(\frac{\partial u_z}{\partial x} - \frac{\partial u_x}{\partial z}\right) - \frac{\partial}{\partial y}\left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x}\right)\right\} \qquad (20)$$

and two similar equations for the displacements in the y and z directions. In the above, Δ denotes the dilatation

$$\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z}\right)$$

or simply divergence $\mathbf{u}$ where $\mathbf{u}$ is the vector whose components parallel to the axes are u_x, u_y and u_z respectively. The three equations in (20) can be combined together and written as a single equation in the form

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = (d_{11} - d_{12}) \nabla^2 \mathbf{u} + d_{12} \text{ grad div } \mathbf{u}$$

$$+ (d_{11} - d_{12} - d_{44}) \text{ curl curl } \mathbf{u} \qquad (21)$$

Since curl curl $\mathbf{u}$ = grad div $\mathbf{u} - \nabla^2 \mathbf{u}$, (21) alternatively becomes

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = d_{44} \nabla^2 \mathbf{u} + (d_{11} - d_{44}) \text{ grad div } \mathbf{u} \qquad (22)$$

We shall now take the *divergence* of both sides of (22). This gives us

$$\rho \frac{\partial^2 \Delta}{\partial t^2} = d_{11} \nabla^2 \Delta \tag{23}$$

The above is in fact the equation of wave propagation in the medium. *Compressional waves are therefore propagated in the solid with the velocity* $\sqrt{d_{11}/\rho}$.

Performing next the operation of *curl* on both sides of (22), and writing ω for curl **u**, one gets

$$\rho \frac{\partial^2 \omega}{\partial t^2} = d_{44} \nabla^2 \omega \tag{24}$$

equation (24) therefore shows *that equivoluminal or distortional waves are propagated in the medium with the velocity* $\sqrt{d_{44}/\rho}$.

It will be noticed that the velocities of propagation of both the longitudinal and transverse waves determine the constants d_{11} and d_{44} only, and do not involve the constant d_{12} at all. On the other hand, d_{44} does not make its appearance in the modulii determinable by static homogeneous strains.

7. Summary

The notions regarding stresses and strains adopted in the classical theory of elasticity are critically examined. The neglect of rotations in the analysis of strain and of torques in the analysis of stress characteristic of that theory is shown to be unjustifiable. A reformulation of the stress-strain relationships taking account of these factors leads to the result that an isotropic solid has *three* independent elastic constants and not *two* as hitherto supposed. Two of these three constants determine the velocities of propagation respectively of longitudinal and transverse waves in the solid. The latter of them does not make its appearance in any observations involving only homogeneous strains nor does it appear in the formulae for the bulk modulus, Young's modulus and Poisson's ratio obtained in the present paper.

8. References

1. Love, A. E. H. .. *The Mathematical Theory of Elasticity.*
2. Webster, A. G. .. *The Dynamics of Particles and of Rigid, Elastic and Fluid Bodies.*
3. Poynting, J. H. and Thompson, J. J. *A Text Book of Physics : Properties of Matter.*
4. Southwell, R. V. .. *An Introduction to the Theory of Elasticity* (Oxford, 1936) (Chapters I, VIII, IX and X).

THERMAL EXPANSION OF BORIC ACID

By M. A. Lonappan

(Department of Physics, University of Madras, Guindy, Madras-25)

Received June 30, 1955

(Communicated by Prof. G. N. Ramachandran, F.A.SC.)

Introduction

The present investigation is in continuation of earlier measurements of thermal expansion of crystals having O_3 groups. The expansion coefficients of potassium chlorate (monoclinic) and potassium nitrate (orthorhombic) have been already determined (Lonappan, 1955 *a*, *b*). Orthoboric acid (H_3BO_3) is triclinic and crystallizes in the class $C_i - \bar{1}$ and belongs to the space group $P\bar{1}$. The unit cell containing four molecules has the dimensions $a = 7{\cdot}039$ Å, $b = 7{\cdot}053$ Å, $c = 6{\cdot}578$ Å, $\alpha = 92{\cdot}58°$, $\beta = 101{\cdot}17°$ and $\gamma = 119{\cdot}83°$ (Zachariasen, 1954). Since the crystal is triclinic none of the principal axes of the ellipsoid of expansion need coincide with any of the crystallographic axes. For the complete determination of the ellipsoid of expansion therefore, the principal expansions as well as the orientation of the principal directions with respect to a co-ordinate system in the crystal have to be obtained. This has been achieved by measuring the variation of the expansion coefficient with direction in three zones. The present study has been made for a range of temperature 30 to 80° C. Orthoboric acid on heating changes into metaboric acid at about 100° C. and on further heating changes into tetraboric acid at about 140° C. (Partington, 1946). Hence the expansion study could not be extended to higher ranges of temperature.

This appears to be the first time that an X-ray method has been adopted for measuring the thermal expansion of a triclinic crystal. Only one other triclinic crystal has been studied earlier, namely, copper sulphate by Sreedhar (1953) using Fizeau's optical method. In his study, however, only the minimum number of measurements necessary for the complete evaluation of the elements of the expansion ellipsoid were made. In the present study, a large number of extra measurements have been obtained and the estimated probable errors are quite small.

2. Experimental Details

Orthoboric acid usually crystallizes in the form of plates; but occasionally some needle-shaped crystals with the *c*-axis as needle axis are also

formed, the well-developed faces parallel to the needle axis being usually $a(100)$, $p(110)$ and $q(1\bar{1}0)$ (Groth, 1910). These indices are with reference to the axes adopted by Groth, for which

$$a:b:c = 1{\cdot}7329:1:0{\cdot}9228$$

$$\alpha = 92°\ 30',\ \beta = 104°\ 25',\ \gamma = 89°\ 49'$$

However, the structure has a pseudo-hexagonal symmetry about the c-axis and this is represented in the unit cell adopted by Zachariasen (1934, 1954) for which

$$a:b:c = 0{\cdot}9980:1:0{\cdot}9327$$

$$\alpha = 92°\ 35',\ \beta = 101°\ 10',\ \gamma = 119°\ 50'$$

The b- and c-axes of Zachariasen are identical with those of Groth, while his a-axis has indices $\frac{1}{2}[1\bar{1}0]$ referred to Groth's axes. Denoting the faces by capital letters when referred to Zachariasen's cell, the well-developed faces in the needle-shaped crystals are A (100), B (010) and Q $(1\bar{1}0)$. In all the discussions hereafter, all the indices will be with reference to Zachariasen's unit cell.

It is necessary to make measurements of expansions along directions lying in three different zones (the three zone-axes being non-coplanar) to obtain completely the elements of the expansion ellipsoid. In the X-ray method adopted by the author, it is possible to measure the expansion along the normals to various planes lying in a single zone by obtaining the rotation photographs about this zone axis at two different temperatures. The details are given in the earlier papers (Lonappan, 1955 *a*, *b*). Consequently, rotation photographs of the zero layer were taken about the *three* zone axes [100], [010] and [001] using a Unicam 19 cm. high temperature camera. The [001] zone was studied by setting the crystal with its needle axis along the rotation axis of the camera. Usually, no crystals are formed with a- or b-axis as needle axis. For obtaining the rotation photographs about the other two zones, these crystals (with c as needle axis) were suitably oriented on the camera. For example, to set the [010] axis along the axis of the camera, the crystal was oriented so that the line of intersection of the faces A (100) and C (001) is parallel to the axis of rotation.

In each zone, the spacings of the high-angle reflections for values of $\theta > 65°$ were measured accurately, as described earlier, at both temperatures and the corresponding coefficients were calculated. The indices of the reflections, determined by the reciprocal lattice diagrams, were confirmed by taking Weissenberg photographs of the crystal set so as to

give the required axis as the axis of rotation. The thermal expansions perpendicular to a number of crystallographic planes in the zone concerned were thus determined. The vapour pressure of the crystal is very high even at room temperature and it is still higher at higher temperatures. The crystals were therefore found to sublime away rapidly after mounting. The recording of the photographs with the crystals had therefore to be completed in the minimum period possible.

3. METHOD OF CALCULATION

In the case of the [001] zone, which was the first zone to be studied, four high-angle reflections were measured. The best values for the maximum and minimum of the expansion coefficient in this zone and the inclination of the direction of the maximum expansion with the a^*-axis were determined by calculation using the method of least squares, as described in the case of potassium chlorate for the [010] zone (Lonappan, 1955 *a*). In the [010] zone, four high-angle reflections were measured. Along with these, the value of thermal expansion along the a^* direction obtained from the study of the previous zone was also taken and the maximum and minimum values of the expansion coefficient and the inclination of the direction of the maximum with a chosen direction (a^*-axis) in the zone were determined. In the third zone, namely the [100] zone, six high-angle reflections could be measured. These, along with the values of the thermal expansion coefficients along the b^* and c^* directions (obtained from the study of the other two zones), were utilised to calculate the maximum and minimum values of the expansion coefficient in this zone and the inclination of the direction of the maximum with the c^*-axis. The measured and calculated values for the three zones are shown in Table I. The maximum and minimum values of the coefficient of expansion and the inclination of the maximum with a chosen direction are given in Table II for each of the three zones.

In order to determine completely the ellipsoid of expansion in the case of a triclinic crystal, the values of α along six general directions are required. Six representative data were therefore obtained from the above three zones. In order to utilise these, it is necessary to have an orthogonal system of co-ordinate axes in the crystal. The system Ox, Oy and Oz chosen is indicated in the stereographic projection in Fig. 1 and is related to the crystallographic axes as follows:—

Ox is taken normal to the c plane, *i.e.*, parallel to c^*-axis

Oy lies in the c^*-a^* plane and is perpendicular to Ox

Oz is perpendicular to Ox and Oy and the three together form a right-handed system.

TABLE I

Measured thermal expansion coefficients of the reflections in [001], [010] *and* [100] *zones*

Sl. No.	Indices of the reflections	With reference to OXYZ system			$\alpha \times 10^6$ (measured)	$\alpha \times 10^6$ (calculated)
		L	M	N		
1	$\bar{4}$ 9 0	·1966	·8788	·4384	10·1	9·1
2	7 1 0	·2419	·5519	·7986	20·3	20·8
3	8 $\bar{2}$ 0	·1794	·2504	·9511	18·1	17·8
4	2 6 0	·2924	·9763	·2588	19·4	19·1
5	0 0 8	·9897	·0218	·1392	250·4	250·9
6	7 0 $\bar{5}$	·4120	·5000	·7547	48·9	48·7
7	7 0 1	·3420	·4226	·8387	36·8	36·9
8	7 0 $\bar{4}$	·2979	·5150	·7986	26·0	28·6
9	0 7 $\bar{5}$	·3584	·9336	·0436	30·7	29·7
10	0 6 4	·7071	·7030	·0610	126·8	126·2
11	0 0 8	·9897	·0218	·1392	251·4	250·9
12	0 7 2	·5075	·8639	·0436	65·4	63·2
13	0 7 $\bar{4}$	·2546	·9681	·0349	13·8	13·2
14	0 7 1	·3987	·9182	·0262	40·1	37·6

TABLE II

Maximum and minimum values of the coefficient of thermal expansion and inclination of the direction of maximum for the three zones

Zone	Thermal expansion $\times 10^6$		Inclination of direction of maximum expansion
	Maximum value	Minimum value	
[001]	21·8	7·3	19° 17′ to a^*
[010]	250·8	7·2	76° 39′ to a^*
[100]	254·0	−2·9	6° 22′ to c^*

The direction cosines of the crystallographic axes a, b, c as well as the axes of the reciprocal lattice (a^*, b^*, c^*) with respect to this co-ordinate system are given in Table III.

TABLE III

Direction cosines of crystallographic axes and reciprocal lattice axes with respect to the co-ordinate system Oxyz

Direction	*l*	*m*	*n*
a	0	0·8704	−0·4924
b	0	0	1·000
c	0·9659	−0·2588	−0·0436
*a**	0·2493	0·9685	0
*b**	0·1662	0·4924	0·8557
*c**	1·000	0	0

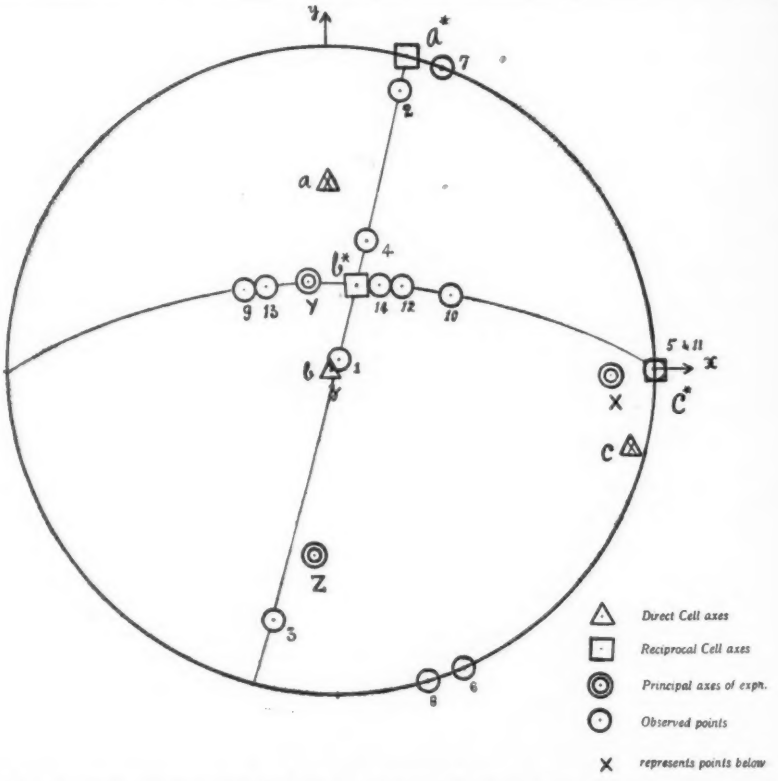


FIG. 1. Stereographic projection of the various directions involved in the present study. Represented here are: (1) the system of co-ordinate axes O*xyz*; (2) the direct cell axes, *a*, *b*, *c*; (3) the reciprocal cell axes *a**, *b**, *c**; (4) the principal axes of expansion OX, OY, OZ, and (5) the directions (1–14) along which the thermal expansion coefficients were measured.

Suppose α is the coefficient of expansion along a direction (l, m, n). Then the general form of α is

$$\alpha = al^2 + bm^2 + cn^2 + 2\,fmn + 2\,gnl + 2\,hlm \tag{1}$$

If $r = 1/\sqrt{\alpha}$ is plotted as a polar diagram in three dimensions, the figure would in general be a conicoid whose equation is

$$ax^2 + by^2 + cz^2 + 2\,fyz + 2\,gzx + 2\,hxy - 1 = 0 \tag{2}$$

If OX, OY, OZ are the principal axes of this figure‡ and L, M, N are the direction cosines of a general direction referred to the axes OXYZ, then the expression for α takes the form

$$\alpha = a_{11}\mathrm{L}^2 + a_{22}\,\mathrm{M}^2 + a_{33}\,\mathrm{N}^2 \tag{3}$$

where a_{11}, a_{22}, a_{33} are the principal expansion coefficients. The corresponding equation to the conicoid becomes

$$\frac{\mathrm{X}^2}{\mathrm{A}^2} + \frac{\mathrm{Y}^2}{\mathrm{B}^2} + \frac{\mathrm{Z}^2}{\mathrm{C}^2} = 1,$$

where

$$\mathrm{A}^2 = 1/a_{11},\ \mathrm{B}^2 = 1/a_{22},\ \mathrm{C}^2 = 1/a_{33} \tag{4}$$

The problem therefore reduces to finding the directions of the principal axes of the ellipsoid such that equation (2) is reduced to the form of equation (4). This can be done by forming the discriminating cubic (Bell, 1931) and solving it.

Writing equation (4) in the form

$$\lambda_1\mathrm{X}^2 + \lambda_2\mathrm{Y}^2 + \lambda_3\mathrm{Z}^2 = 1 \tag{5}$$

it can be shown that λ_1, λ_2, λ_3 are the roots of the equation.

$$\lambda^3 - \alpha\lambda^2 + \beta\lambda - \gamma = 0$$

where

$$\alpha = a + b + c,$$

$$\beta = ab + bc + ca - f^2 - g^2 - h^2$$

and

$$\gamma = \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix} \tag{6}$$

‡ Capital letters X, Y, Z are used to indicate the principal axes, as distinct from x, y, z which denote the co-ordinate system of reference.

The cubic can be solved by Cardan's method. The roots of the discriminating cubic themselves then give the principal expansion coefficients.

The orientation of each principal axis can be determined by substituting the appropriate root (λ_i) in the following set of equations (Bell, 1931) and solving for l_i, m_i, n_i.

$$\begin{aligned} (a - \lambda_i)\, l_i + \quad & hm_i + gn_i \quad = 0 \\ hl_i \quad & + (b - \lambda_i)\, m_i + fn_i = 0 \\ gl_i \quad & + fm_i + (c - \lambda_i)\, n_i = 0 \end{aligned} \tag{7}$$

4. RESULTS OF THE INVESTIGATION

The six representative values used for the calculation of the principal expansion coefficients were

(1) along the x-axis
(2) at 45° to the x-axis in the xy plane
(3) along the y-axis
(4) along the direction of the maximum in the a^*-b^* plane
(5) at 45° to the maximum in the same plane and
(6) at 45° to c^* direction in the c^*-b^* plane

In order to make full use of all the observed data, these representative values were calculated from the data given in Table II, as these give the best fit with observations in each zone. Table IV gives the orientation and magnitude

TABLE IV

Thermal expansion α and direction cosines for the six values used for the final calculation

$\alpha \times 10^{-6}$	l	m	n
250·7	1·00	0	0
124·4	0·7071	0·7071	0
7·3	0	1·00	0
21·8	0·2498	0·9104	0·3299
14·6	0·1476	0·4100	0·9001
153·8	0·7071	0·3518	0·6134

of the representative values used. These yield six linear equations of the type of equation (1) in a, b, c, f, g, h. Solving these, we have, omitting the factor 10^{-6},

$$a = 250{\cdot}7,\ b = 7{\cdot}29,\ c = 5{\cdot}074$$

$$f = -7{\cdot}017,\ g = 35{\cdot}722 \text{ and } h = -4{\cdot}595.$$

The corresponding discriminating cubic is given by

$$\lambda^3 - 263{\cdot}064\lambda^2 + 1790{\cdot}23\lambda + 10176{\cdot}9 = 0$$

whose solutions are

$$\lambda_1 = 255{\cdot}913,\ \lambda_2 = -3{\cdot}674,\ \lambda_3 = 10{\cdot}826.$$

These give the principal coefficients of expansion. The data regarding the orientation of the principal axes of the ellipsoid with respect to Ox, Oy Oz are given in Table V. The orientation of the principal axes are expected to be correct to 1°, although the exact probable error is difficult

TABLE V

Data regarding principal axes of the ellipsoid of expansion

Value of principal expansion $\times 10^6$	−3·674	10·826	255·913
l	−0·1113	−0·0902	0·9896
m	0·5022	−0·8644	−0·0226
n	0·8576	0·4947	0·1415
Angle with Ox	96° 23′	95° 11′	8° 16′
Angle with Oy	59° 51′	149° 48′	91° 18′
Angle with Oz	30° 58′	60° 21′	81° 52′

to calculate. The measured data as well as the orientations of the various axes used in this study are also indicated in the stereographic net in Fig. 1. The agreement between the observed and calculated values for the three zones are brought out in Figs. 2 *a*, *b* and *c*, which represent the polar diagrams of thermal expansion for the three zones. The continuous curves represent the variations to be expected theoretically and the circles represent the observed values, which are found to be close to the continuous curves. The probable errors of the principal values of expansion were estimated

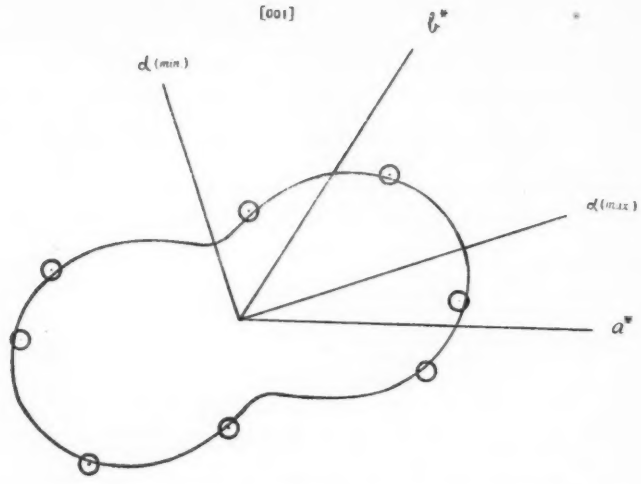


FIG. 2 *a*. Variation of expansion coefficient α with direction in the [001] zone. The continuous curve represents the theoretical variations to be expected and the circles represent the observed values.

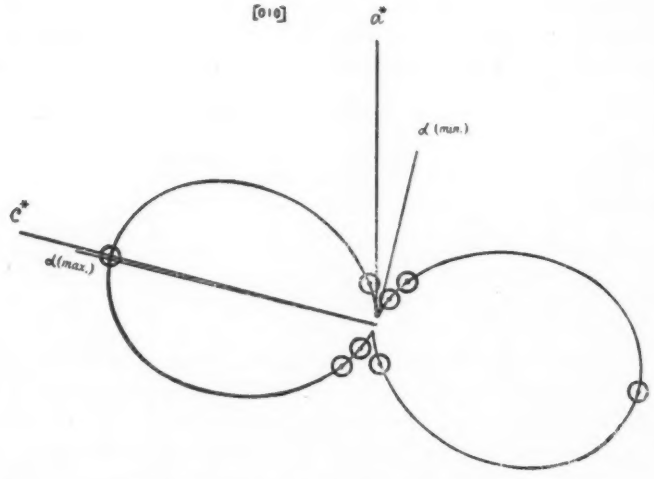


FIG. 2 *b*. Variation of expansion coefficient α with direction in the [010] zone. The continuous curve represents the variations to be expected theoretically and the circles represent the observed values.

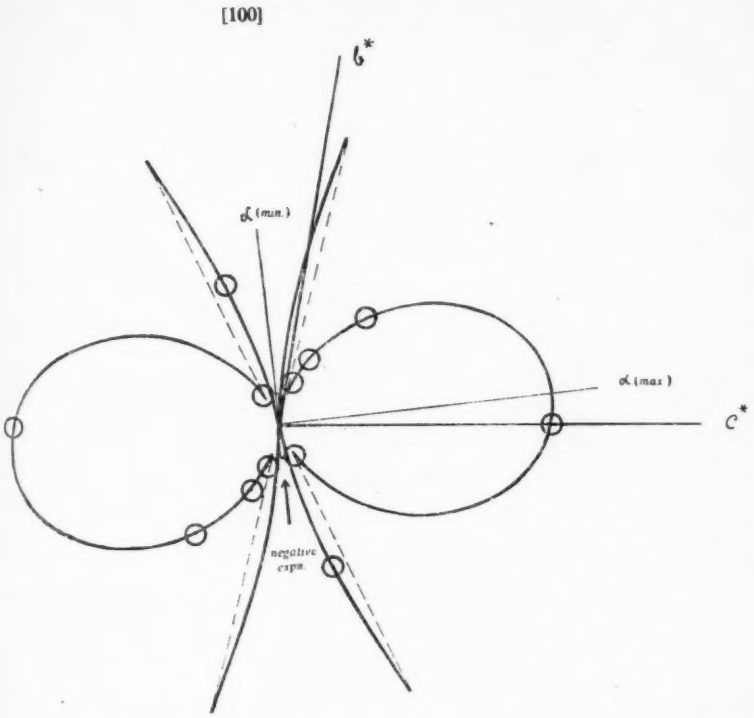


FIG. 2 *c*. Variation of expansion coefficient α with direction in the [100] zone. The continuous curves represent the variations to be expected theoretically and the circles represent the observed values. The two small loops represent the region where the value of α is negative. The portions of the curve corresponding to 20° on either side of the minimum are represented on a magnified scale, 10 times larger than the rest of the diagram.

from the differences between the calculated and observed values in Table I. The final values are

$$\alpha_{11} = -3{\cdot}67 \pm 0{\cdot}6,\ \alpha_{22} = 10{\cdot}83 \pm 1{\cdot}0,\ \alpha_{33} = 255{\cdot}9 \pm 1{\cdot}0 \times 10^{-6}.$$

5. DISCUSSION

It is interesting to note that the three principal values are quite different from one another, the highest being about 250 and the lowest -3×10^{-6}. The direction of maximum expansion is close to the normal to the O_3 planes, as has been found with other crystals with planar O_3 groups. The variation in the plane of the O_3 group of about 14×10^{-6} is of the same order as in the case of aragonite and potassium chlorate; but no negative value for expansion is given by any of these. Calcite however has a negative value of

-6×10^{-6} in the plane of the O_3 group. The direction of maximum negative expansion in boric acid is almost perpendicular to the *a*-axis in the *c* plane. According to the structure of boric acid the shortest OH· · ·O hydrogen bonds, *i.e.*, the strongest bonds, are perpendicular to the *a*-axis. The average length of the two bonds in this direction is 2·712 Å. while the corresponding values in the other two directions at $\pm$ 120° to it are 2·725 and 2·725 Å. It is reasonable to expect that the smallest expansion would occur in the direction of the strongest bond, as is found to be the case.

The highest value of thermal expansion is nearly perpendicular to the plane of the O_3 group. However, it is tilted by about 8° towards the *b*-axis. Orthoboric acid has a layer structure almost parallel to the *c* plane occurring at hieghts of $\frac{1}{4}$ *c* and $\frac{3}{4}$ *c*, so that only Van der Waals' forces exist between them, which is exhibited by the perfect cleavage along the *c* plane. This accounts for the very large value of the expansion almost perpendicular to the *c* plane. However, the BO_3 planes are not exactly parallel to the *c* plane. The inclination of the different groups in the unit cell are different and it has not been found possible to correlate the exact direction of maximum expansion (namely its tilt from the normal to the *c* planes) with the orientation of the individual O_3 groups.

Another crystal for which negative expansion has been reported is hydrargillite (Megaw, 1933). Even though hydrargillite $Al(OH)_3$ has a layer structure and has the group $(OH)_3$ as in the case of boric acid $B(OH)_3$ the details of the structure are quite different. Hydrargillite contains pairs of closely packed planes of oxygen atoms with a layer of aluminium in between. Each aluminium atom is surrounded by six oxygen atoms in octahedral coordination. In view of this, the expansion of hydrargillite is not maximum normal to the layers of atoms parallel to the *c* plane. The maximum occurs at an angle of 45° to the c^* direction in the c^*-a^* plane. The situation is very different with boric acid. Consequently, the idea of the relative slipping of planes leading to a negative expansion coefficient, suggested by Megaw in the case of hydrargillite, cannot be applied to boric acid.

It may be added that even a cubic crystal such as α-AgI, is known to have a negative thermal expansion (Fizeau, 1867; Jones and Jelen, 1935; Cohen and Bredee, 1937), which has not been properly explained. Another case of negative thermal expansion is monoclinic platinum phthalocyanine (Ubbelohde and Woodward, 1942–43) for which also no adequate explanation was put forward. Boric acid is thus the fifth example of a crystal exhibiting thermal *contraction* along some direction in it.

The author wishes to record his deep indebtedness to Professor G. N. Ramachandran for the invaluable suggestions he gave and the keen interest he took in the course of this study.

Summary

The principal coefficients of expansion and the orientation of the ellipsoid of expansion have been determined for orthoboric acid, a triclinic crystal, for the range of temperatures 30 to 80° C. by an X-ray method. The anisotropy of expansion is extremely large, the maximum expansion being 256 and the minimum -4, $\times 10^{-6}$. The direction of the maximum expansion coefficient is close to the normal to the *c* plane, to which all the O_3 groups are closely parallel. The occurrence of a negative expansion is a special feature of this crystal, the direction of which is found to be parallel to the shortest hydrogen bonds. This is the first time that the thermal expansion of a triclinic crystal has been fully studied by an X-ray method.

References

1. Bell, R. J. T. .. *Co-ordinate Geometry of Three Dimensions*, Macmillan and Co., London, 1931, p. 208.
2. Cohen, E. and Bredee, H. L. *Proc. K. Akad. Amsterdam*, 1936, **39**, 358.
3. Fizeau, H. .. *Pogg. Ann.*, 1867, **132**, 292.
4. Groth, P. .. *Chemische Kristallographie*, 1910, **1**, 121.
5. Jones, G. and Jelen, F. C. *Journ. Am. Chem. Soc.*, 1935, **57**, 2532.
6. Lonappan, M. A. .. *Proc. Phy. Soc.*, 1955 *a*, **68B**, 75.
7. ——— .. *Proc. Ind. Acad. Sci.*, 1955 *b*, **41A**, 239.
8. Megaw, H. D. .. *Proc. Roy. Soc.*, 1933, **142A**, 198.
9. Partington, J. R. .. *Text-Book of Inorganic Chemistry*, Macmillan and Co., London, 1946, p. 717.
10. Sreedhar, A. K. .. *J. Ind. Inst. Sci.* 1953, **35A**, 17.
11. Ubbelohde, A. R. and Woodward, I. *Proc. Roy. Soc.*, 1942–43, **181A**, 415.
12. Zachariasen, W. H. .. *Zeits. f. Krist*, 1934, **88**, 150.
13. ——— .. *Acta. Cryst.*, 1954, **7**, 305.

UNIVERSITY OF MICHIGAN LIBRARIES

ANALYSIS OF τ-MESONS

By P. S. Goel and K. A. Neelakantan

(Tata Institute of Fundamental Research, Bombay 1)

Received June 20, 1955

(Communicated by Professor Bernard Peters, F.A.SC.)

Abstract

We describe in this paper measurements made on the decay products of 11 τ-mesons observed in large nuclear emulsion block detectors. Out of the 33 charged decay products, 27 have been arrested in the block, and were identified as π-mesons. The charge of the τ-meson was found to be positive in 6 cases. In one case the charge of the τ-meson is possibly negative and in 4 cases it could not be determined. Omitting one τ-meson in which a high energy γ-ray is emitted and which has been reported earlier[1] the weighted mean Q-value of the remaining 10 τ-mesons is:

$$Q_\tau = 76{\cdot}3 \pm 0{\cdot}3 \text{ MeV}$$

which gives the mass of the τ-meson as:

$$m_\tau = 968{\cdot}7 \pm 0{\cdot}6\, m_e$$

This value is slightly higher than the mean value $965{\cdot}5 \pm 0{\cdot}7\, m_e$ compiled by Amaldi *et al.*[2] from measurements of various laboratories.

We have so far observed 11 cases of disintegration of τ-mesons at rest into charged π-mesons. These events occurred in three emulsion block detectors whose construction has been described elsewhere.[3, 4] Of these 11 τ-mesons, 7 were found by tracing π-mesons from the end of their range back towards their origin; the remaining 4 τ-mesons were discovered during systematic scanning. Ten of the 11 τ-mesons could be traced back to the nuclear explosion in which they originated.

Of the 33 charged decay products, 27 came to rest in the emulsion blocks, and were identified as π-mesons ($18\pi^+$, $8\pi^-$, and 1 more π-meson with a probably negative charge). The charge of the τ-meson was positive in 6 cases. In 1 case (τ_9) observational conditions at the end of one of the π-meson tracks are unfavourable. The π-meson becomes suddenly very steep near the end of its range and stops after travelling another 712 μ in the emulsion. We have not been able to detect any decay electron at the

point where the particle stopped nor any point where change of direction or of grain density suggests that the π-meson decayed into a μ-meson. Hence this π-meson might be negative. If this interpretation is accepted τ_9 gives rise to two negative and one positive π-meson.

Table I gives the results of measurements on all 11 events. τ_1, τ_2 and τ_3 have already been reported.[5] Their Q-values given in Table I are slightly different from those reported earlier, because we have based all our analyses on a slightly modified range energy relation.[6]

τ_4 is abnormal since nearly 50% of the available kinetic energy is carried away by a γ-ray and not by the three π-mesons. This event has been discussed in detail in an earlier paper by Daniel and Yash Pal.[1] τ_5 and τ_8 suffer inelastic collisions before they come to rest. These collisions have been discussed in a previous paper by Daniel and Lal,[7] but the data on the decay products of these τ-mesons have not been published before.

The first four columns in Table I give information on the parent particle. The τ-meson number is given in column 1, column 2 gives the description of the nuclear event in which the τ-meson originates (we use here the nomenclature of Brown *et al.*[8]). The range of the τ-meson before it comes to rest and the energy of the τ-meson at emission are given in columns 3 and 4 respectively.

The next 4 columns of Table I give information on the decay products. The charge of the π-meson is given in column 5 when it can be inferred from its behaviour at rest ($\mu - e$ decay or capture star). When the charge of the π-meson is unknown a question mark is inserted.

The range of the π-mesons is given in column 6. All range measurements were carried out independently by two observers. The symbol (t) in column 6 signifies that the particle comes to rest in the block and its total range has been measured. The symbol (o) indicates that the particle escapes and only the observed portion of the range is given.

The energy of the π-meson is listed in column 7. The range-energy curve which we used[6] is based on a flat μ-meson range of $574{\cdot}5 \pm 7{\cdot}7\,\mu$ while in our detector the mean range of flat μ-mesons obtained from the decay of π-mesons at rest is $(579{\cdot}9 \pm 3{\cdot}6)\,\mu$. Hence we have reduced the observed ranges by the ratio 574·5/579·9, before using the range-energy relation.

The angle between the tracks is given in column 8. The Q-values and their estimated errors are obtained as follows: If all the three π-mesons come to rest in the block, the Q-value was obtained by merely adding the

UNIVERSITY OF MICHIGAN LIBRARIES

TABLE I

1	2	3	4	5	6	7	8	9
	Parent Particle			Secondary Particles				
No.	Origin	Range (cm)	Energy (MeV)	Sign of charge	Range in μ	Energy (MeV)	True angles (degrees)	Q-value (MeV)
1	21+ 2 α	·0367	6·4	1 + 2 + 3 (−)	5262 (t) 11245 (t) 4600 (o)	16·77 26·12 (33·40 ± ·70)	$\alpha = \sphericalangle 2\cdot3 = 137\cdot20$ $\beta = \sphericalangle 3\cdot1 = 121\cdot85$ $\gamma = \sphericalangle 1\cdot2 = 100\cdot80$	76·24 ± 1·03
2	6+ 0p	·665	31·7	− + ?	4638 (t) 8636 (t) 3364 (o)	15·45 22·29 (38·20 ± 1·00)	$\alpha = 141\cdot60$ $\beta = 132\cdot90$ $\gamma = 85\cdot50$	75·46 ± 1·69
3	13+10 α	·747	33·6	+ ? ?	1115 (t) 3000 (0) 11820 (o)	6·85 (29·98 ± 1·08) 39·05	$\alpha = 161\cdot80$ $\beta = 118\cdot80$ $\gamma = 79\cdot30$	75·88 ± 2·59
4	9+ 1 n 0p	8·700	145·9	+ + (−) γ-ray	124 (t) 3921 (t) 2500 (o)	1·85 13·60 (30·6 ± 2·2) 32·10	$\alpha = 128\cdot85$ $\beta = 56\cdot00°$ $\gamma = 146\cdot80$	78·2 ± 4·9
5*	8+10p	1·315	47·0	− ? +	1050 (t) 13792 (t) 24294 (t)	6·49 29·02 40·52	$\alpha = 158\cdot74$ $\beta = 127\cdot25$ $\gamma = 74\cdot01$	76·03 ± ·88
6	26+ 2p	4·100	88·6	+ − +	5294 (t) 12103 (t) 16861 (t)	16·90 27·07 32·84	$\alpha = 136\cdot95$ $\beta = 118\cdot40$ $\gamma = 104\cdot61$	76·81 ± ·82
7	22+ 5p	2·200	62·19	+ + −	3288 (t) 5862 (t) 30777 (t)	12·62 17·88 46·50	$\alpha = 159\cdot70$ $\beta = 154\cdot90$ $\gamma = 45\cdot60$	77·00 ± ·90
8*	8+ 1p	1·150	44·0	+ + −	323 (t) 16380 (t) 22490 (t)	3·35 32·14 38·71	$\alpha = 166\cdot15$ $\beta = 122\cdot63$ $\gamma = 71\cdot15$	74·20 ± ·88
9	12+ 6p	·970	38·71	− + −(?)	2140 (t) 13583 (t) 21650 (t)	9·69 28·64 38·28	$\alpha = 153\cdot20$ $\beta = 123\cdot85$ $\gamma = 82\cdot95$	76·61 ± ·86
10	The Primary could not be followed completely			− ? +	2951 (t) 6508 (o) 24522 (t)	11·60 (25·21 ± ·13) 40·71	$\alpha = 150\cdot00$ $\beta = 130\cdot95$ $\gamma = 79\cdot00$	77·52 ± ·87
11	25+11 n	7·600	125·82	+ + −	1108 (t) 12897 (t) 25671 (t)	6·72 27·94 41·78	$\alpha = 159\cdot45$ $\beta = 129\cdot90$ $\gamma = 70\cdot63$	76·44 ± ·89

energies of the three π-mesons. The indicated error on the Q-value contains only the effect due to straggling. We have calculated the effect of straggling on the basis of the formula given by Symon.[9] But we have increased the theoretical values by 20% which seems to be required to obtain agreement between Symon's calculations and the experimental straggling value of Fry and White.[10]

If one of the mesons escapes, Q-values are calculated from the remaining 5 observables (2 momenta and the 3 angles). By choosing 1 of the momenta and any 2 of the remaining observables, one obtains 5 different Q-values. The Q-values given in Table I represent the average of these 5 determinations and the error given is the maximum deviation of any of these 5 values from the average.

The most serious uncertainty arises from variations in the thickness of individual emulsion sheets. The method by which we have tried to minimise this effect is given in the Appendix.

Conclusions

Omitting the 4 body decay τ_4, the weighted average Q-value was obtained by choosing weight factors inversely proportional to the square of the error attached to each value. Our best Q-value is:

$$Q_\tau = 76{\cdot}3 \pm 0{\cdot}3 \text{ MeV}$$

and

$$m_\tau = 968{\cdot}7 \pm 0{\cdot}6\, m_e{}^*$$

This value is about 1·6 MeV higher than the value obtained by Amaldi[2] on the basis of data reported by many laboratories at the Padova Conference on Elementary Particles in 1954.

Figure 1 shows the distribution of our values together with those from other laboratories.

Omitting the abnormal τ_4 we have computed the ratio $E\pi^-/Q_\tau$ for those cases in which the charge of the τ-meson is known to be positive and in which the negative π-meson has been identified. The mean value

$$\left\langle \frac{E\pi^-}{Q\tau} \right\rangle = 0{\cdot}3360 \pm 0{\cdot}0026$$

indicates complete symmetry in the energy distribution among the decay products.

* m_τ is calculated from the relation $m_\tau = 2m_{\pi^+} + m_{\pi^-} + Q$, where m_{π^+} and m_{π^-} are those given by Smith, Birnbaum and Barkas.[11]

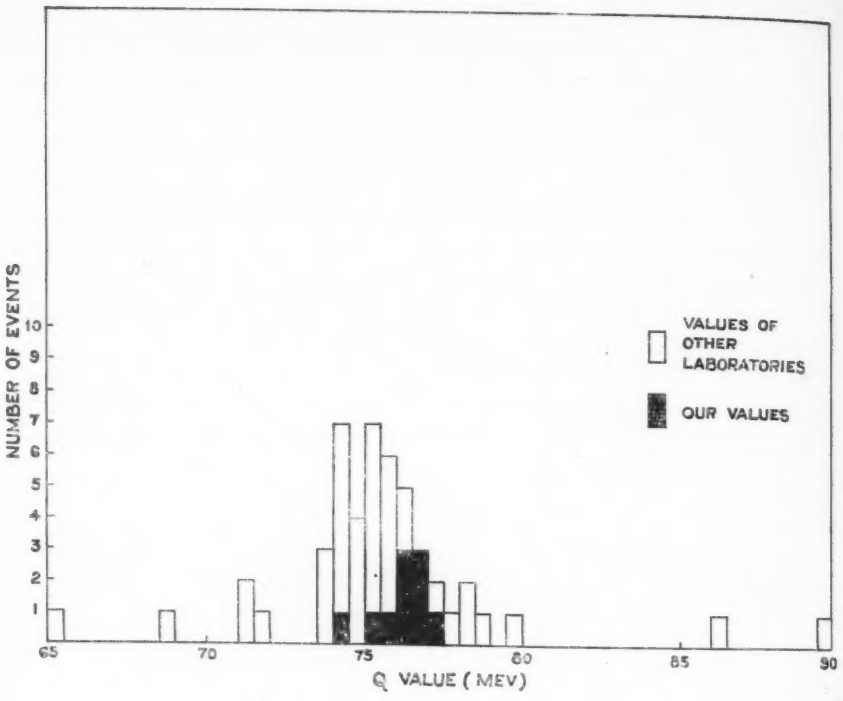


FIG. 1

ACKNOWLEDGEMENTS

We have great pleasure in thanking Professor B. Peters for his continued interest and guidance throughout this work.

We also express our thanks to Mr. D. Lal, for his active help and to Dr. R. R. Daniel for helpful discussions. Lastly we thank Miss A. L. Damany and Miss T. M. Purohit for observation of some of the events.

APPENDIX

An accurate determination of the range of particles and hence their energy, requires a knowledge of the emulsion thickness before processing. A private communication from Ilford Limited states that variations as high as 10% can occur in the thickness, between different parts of the same emulsion sheet, as well as between different emulsion sheets although usually variations are much lower. In the construction of two big emulsion blocks, we have used five different batches of emulsion sheets manufactured on

different dates. Each batch consisted on the average from 50–100 sheets. Their mean thickness was determined as follows:—

We measured the range of 50 flat μ-mesons emitted from π-mesons at rest and of 14 steep μ-mesons which occur in a single batch of emulsions. The average range of the steep μ-mesons depends on the assumed emulsion thickness d. We chose for the average emulsion thickness in the batch that value of d which makes the mean range of flat and steep μ-mesons identical.

The relative mean emulsion thickness in different batches was obtained by determining separately the mean projected length of heavy primary nuclei which traversed plates belonging to different batches. In this way we found that our emulsion blocks were composed of emulsions belonging to 5 different manufacturing batches with mean thickness of 600 μ, 637 μ, 650 μ, 660 μ and 667 μ respectively.

References

1. R. R. Daniel and Yash Pal, *Proc. Ind. Acad. Sci.*, 1954, **40** (3), 114.
2. E. Amaldi, E. Fabri, T. F. Hoang, W. O. Lock, L. Scarsi, B. Touschek and B. Vitale, *Nuo. Cim.*, 1954, **12**, (9), *Supple.* 2, 419.
3. D. Lal, Yash Pal and B. Peters, *Proc. Ind. Acad. Sci.*, 1953, **38** (4), 277.
4. R. R. Daniel, G. Friedmann, D. Lal, Yash Pal and and B. Peters, *Ibid.*, 1954, **40** (4), 151.
5. D. Lal, Yash Pal and B. Peters, *Ibid.*, 1953, **38** (5), 398.
6. R. R. Daniel, E. C. George and B. Peters, *Ibid.*, 1955, **41** (2), 45.
7. —— and D. Lal .. *Ibid.*, 1955, **41** (1), 15.
8. R. H. Brown, U. Camerini, P. H. Fowler, H. Heitler, D. T. King and C. F. Powell, *Phil. Mag.*, 1949, **40**, 862.
9. K. R. Symon .. Harvard University *Thesis* (1948); Quoted in: *High Energy Particles* by B. Rossi, Prentice Hall, Inc., New York, 1952, pp. 37.
10. W. F. Fry and C. R. White, *Phys. Rev.*, 1953, **90**, 207.
11. F. M. Smith, W. Birnbaum and W. H. Barkas, *Ibid.*, 1953, **91**, 765.

COLORIMETRIC ESTIMATION OF URANIUM WITH AMMONIUM THIOCYANATE AND ITS APPLICATION TO DETERMINATION OF URANIUM IN MINERALS PARTICULARLY MONAZITE CONCENTRATES

By Mahadeo M. Tillu, D. V. Bhatnagar and T. K. S. Murthy

(*Chemistry Division, Atomic Energy Establishment, Bombay*)

Received July 2, 1955

(Communicated by Dr. H. J. Bhabha, F.R.S., F.A.SC.)

Introduction

During analyses of mineral samples for their uranium contents, it was found necessary to use a sensitive colorimetric method with the least number of interferences. The method based on the yellow colour produced by uranyl ions and ammonium thiocyanate in dilute mineral acid solutions, first described by Currah and Beamish[3] for the analysis of uranium in thorium samples showed promise of successful application in the case of low grade uranium ore samples. Gerhold and Hecht[7] have further studied the photometric estimation of small amounts of uranium with potassium thiocyanate. They reported that (i) the colour when developed in hydrochloric acid solution was stable for at least two hours and (ii) the intensity first increased with thiocyanate concentration and then remained constant. A detailed study of this method has been made in this laboratory, using ammonium thiocyanate, stress being laid on its application to estimation of uranium in minerals.

Experimental

Lumetron model 402 EF Colorimeter with M 365 Filter was used for the preliminary studies described below:—

(*a*) *Influence of the concentration of ammonium thiocyanate on the intensity of the colour.*—As reported by Currah and Beamish (*loc. cit.*) the colour intensity increased with thiocyanate concentration with no sign of reaching a maximum. This is contrary to the observations of Gerhold and Hecht who used potassium thiocyanate.

(*b*) *Effect on concentration of acid on the intensity of the colour.*—Solutions were prepared containing 0·2 mg. uranium, 5 ml. of 50% (w/v) ammonium thiocyanate and varying amounts of 8 Normal acid in a total

volume of 25 ml. In the case of HCl and HNO_3, the intensity of the colour increased with acid concentration (up to 2 N total acid concentration) while in the case of sulphuric acid the intensity decreased. Since at higher acid concentrations, thiocyanate might decompose causing errors in the colour measurement, 2·5 ml. of 4 N hydrochloric acid was used for all subsequent work and transmittancy measurements were made immediately after mixing up the solutions. It may be mentioned that using this acid concentration it was found unnecessary to make any pH adjustment as described by Currah and Beamish.

(*c*) *Interference from anions.*—The effect of the following anions has been studied and the maximum amount of each which could be tolerated in 25 ml. solution is given in the following table (the solution contained 0·2 mg. uranium).

Anion	Max. amount permissible
Chloride	500 mg. (NaCl)
Nitrate	500 mg. ($NaNO_3$)
Sulphate	500 mg. (K_2SO_4)
Fluoride	50 mg. (NaF)
Phosphate	100 mg. (NaH_2PO_4)
Tartrate	500 mg. (Tartaric acid)
Citrate	1000 mg. (Citric acid)
Oxalate	200 mg. (Oxalic acid)

(*d*) Mo, V and W seriously interfere. Rare earths diminish the transmittancy slightly. Titanium gives a colour similar to that given by uranium. Al, Ca, Mg do not interefere and 125 mg. ThO_2, 4 mg. Fe and 125 mg. P_2O_5 can be tolerated.

Application of the method for the determination of uranium in minerals

The method described by Harvey[5] was followed for the decomposition of the mineral and subsequent ether extraction of the uranyl nitrate. 50 ml. of distilled water was added to the ether extract and the ether removed by evaporation. The aqueous solution was transferred into a platinum dish and evaporated to dryness. The organic matter was destroyed by igniting

at a low heat and the residue was taken into solution by warming with a few drops of concentrated HCl and the solution was then evaporated to dryness on a water-bath. The residue was dissolved in the least amount of water and transferred to a 25 ml. measuring flask. 2·5 ml. of 4 N HCl, 1 ml. of 20% $SnCl_2$ solution and 10 ml. of 50% ammonium thiocyanate were added and the transmittancy measured against a blank containing the same amounts of reagents and adjusted to 100% transmittancy. A standard curve was prepared by measuring the transmittancy of a set of solutions containing the same amounts of reagents and 0·05–0·6 mg. of uranium. The results on some of the samples are shown below:—

Sample No.	U_3O_8%	
	Thiocyanate method	Peroxide method[9]
1	0·005	0·005
2	0·011	0·010
3	0·024	0·028

Direct estimation in monazite concentrates

Indian monazite sands of which the country has a large quantity invariably contain a certain amount of uranium as one of the ingredients.[11] The difficulty in estimation of uranium in monazite is mainly due to the presence of such heavy metals as Th, Zr, Ti and Rare earths along with considerable amounts of phosphate. The phosphates of some of these metals are relatively insoluble in mineral acid solutions of moderate concentrations and when they precipitate out due to dilution or decreased acidity they carry appreciable amounts of uranium with them. Therefore a preliminary isolation of uranium from these metals and from the other constituents of monazite is necessary before the other colorimetric methods[4, 9, 10] could be applied for its estimation. Though monazite concentrates can be completely decomposed by treatment with hot concentrated sulphuric acid, this method is not usually followed since large amounts of sulphate interfere in the ether extraction of uranyl nitrate which is a frequently used procedure for its preliminary separation. However, a direct colorimetric estimation, which does not necessitate separation of uranium would serve as a quick method for the routine analysis of monazite concentrates. Since ammonium thiocyanate could be used for uranium estimation in dilute mineral acid solutions,

the feasibility of applying this method in the case of monazite concentrates, after decomposing them with sulphuric acid, was investigated. The monazite concentrates used in this work were obtained from the Indian Rare Earths, Ltd., Travancore.

Careful work showed that the residues obtained after decomposing monazite concentrates with sulphuric acid contained negligible amounts of uranium. From preliminary work it was found that in 2·5% sulphuric acid solution the intensity of colour with 0·05 mg. uranium in 25 ml. was adequate for accurate estimation on a Beckman DU Spectrophotometer at 365 mμ.

The analyses of Indian monazite concentrates carried out in this laboratory and the values reported by Bearse[1] and Mellor[8] show that the following constituents are present:—

Thoria	8–10%	Uranium oxide (U_3O_8)	0·3–0·5%
Cerous oxide	27–29%	Lead oxide ..	0·2%
Neodymium oxide ..	~11%	Titania	0·3–0·5%
Praseodymium oxide ..	3–3·5%	Zirconia	0·5–1·0%
		Ferric oxide ..	0·3–0·5%
Samarium oxide ..	3–4 %	Alumina	0·1–0·2%
Lanthanum oxide ..	11–12%	Lime	1·0–2·0%
Yttrium oxide	< 1%	Magnesia	<1·0%
Phosphate (P_2O_5) ..	27–29%	Loss on ignition ..	~0·2%
Silica	~1%		

The results of investigations carried out on the interference of above radicals in the estimation of uranium in 2·5% sulphuric acid solution with thiocyanate are summarised below:—

(*a*) The samples used were found to contain no traces of Mo, V and W the presence of which would have seriously interfered.

(*b*) Upto 125 mg. Th, and 4 mg. Fe and 125 mg. P_2O_5 in 25 ml. did not interfere.

(*c*) Rare earths, added as a mixture obtained from monazite samples, diminished the transmittancy.

(*d*) Alumina, lime and magnesia did not interfere and silica, lead and zirconia would remain insoluble in sulphuric acid solution.

(*e*) Titanium gave a colour with thiocyanate which did not disappear on addition of stannous chloride. Colour intensity due to titanium diminished in the presence of phosphoric acid.

To overcome the interference due to sulphuric acid and rare earths, a suitable blank was prepared containing approximately the same amounts of thorium, rare earths, sulphuric acid and phosphoric acid as in the solution under estimation. This balanced all other interferences except that due to titanium. In another aliquot of the solution titanium was determined and a correction applied to the measured optical density of uranium. The details of the procedure are given below:—

Reagents (*Analar* grade chemicals were used):

Ammonium thiocyanate: 500 gm. of ammonium thiocyanate per 1000 ml. solution.

Stannous chloride: 50 g. of $SnCl_2.2H_2O$ dissolved in 50 ml. concentrated HCl, diluted to 250 ml. with water and filtered.

Sulphuric acid: 2 Normal solution.

Standard solution of uranyl sulphate in 2 N sulphuric acid containing 0·1 mg. U_3O_8 per ml.

Standard solution of titanium sulphute in 2 N sulphuric acid containing 0·1 mg. TiO_2 per ml. of solution.

Blank solution: This was prepared from rare earth oxides and phosphoric acid.

PROCEDURE

1. *Preparation of the "blank" solution.*—A representative sample of monazite was decomposed with sulphuric acid and total thorium and rare earths were separated by repeated (thrice) precipitations as oxalates, to free them from uranium, and finally ignited to oxides. 6·9 g. of the oxide mixture was fumed with 30 ml. of sulphuric acid and after reducing Ce IV and adding 2·7 g. of P_2O_5 (in the form of syrupy phosphoric acid) the solution was diluted to 500 ml. 5 ml. of this solution corresponded to 0·1 g. of monazite.

2. *The calibration curve for uranium.*—To 5 ml. of the 'blank' solution 0·5 to 8·0 ml. of standard uranium solution was added and after addition of 1 ml. of stannous chloride and 10 ml. of thiocyanate reagent the total volume was made upto 25 ml. with 2 N sulphuric acid. Optical density was measured at 365 mμ with the Beckman DU' spectrophotometer after adjusting to 100% transmittancy with a blank solution containing the abovementioned amounts of reagents but no uranium. When concentrations of

uranium were plotted against optical density (Du) a straight line graph was obtained.

3. *Calibration curve for titanium.*—A standard curve showing the relation between titanium concentration and the optical density of the colour produced with thiocyanate was made as in the case of uranium. Measurements were made at 365 mμ. The graph was a straight line upto 0·5 mg. TiO_2 per 25 ml.

4. *Preparation of solution of the sample and the determination of total optical density due to uranium and titanium.*—A 5 g. sample was digested at about 250° C. with 15 ml. of concentrated sulphuric acid, contents being stirred occasionally, until all the monazite had decomposed. The beaker was allowed to cool and about 200 ml. of ice cold distilled water were added while stirring. The contents were then transferred to a 250 ml. volumetric flask and the volume adjusted to the mark. After 1 to 2 hours the solution was filtered through a dry Whatman No. 42 filter into a dry beaker.

5 ml. of the filtrate (corresponding to 0·1 g. of monazite) was pipetted out in a beaker, 9 ml. 2 N sulphuric acid and 1 ml. stannous chloride reagent were added. After 5 minutes 10 ml. of thiocyanate reagent was added and the total optical density (Dtu) due to uranium and titanium was measured as in (2) above.

5. *Correction due to titanium.*—In another 50 ml. of the solution titanium was determined by the classical hydrogen peroxide method by comparing the colour against a standard titanium solution added to 50 ml. of the 'blank' [(1) above]

TiO_2 in 0·1 g. monazite .. .. .. ='T' mg.

Optical Density due to 'T' mg. TiO_2 from (3) above .. .. = Dt

Measured optical density due to Titanium and Uranium .. .. =Dtu

Optical density due to uranium .. .. =Dtu−Dt = Du

From the calibration graph for uranium [(2) above] the amount of U_3O_8 was determined. It was found that 0·1 mg. TiO_2 would give the same optical density as 0·04 mg. U_3O_8.

RESULTS

Sample No.	mg. TiO_2/ 5 ml. 'T'	U_3O_8 %	
		By this method after correcting for titanium	By other methods
1	0·15	0·37	0·38*
2	0·13	0·37	0·38*
3	0·27	0·40	0·38* 0·38†
4	0·23	0·36	0·34†
5	0·22	0·36	0·34†
6	0·15	0·41	0·40†

*By paper column method[2] †By Harvey's method[6]

DISCUSSION

From this study it is clear that ammonium thiocyanate method could be used for the estimation of uranium in low grade uranium ore samples. However, a preliminary separation of the uranium was found necessary and it was done by ether extraction of the nitrates.

For the estimation of uranium in monazite concentrates, no preliminary separation was needed. But a 'blank' as described in the procedure was necessary to balance the interference due to the rare earths, and phosphate. Titanium interferes seriously and since variable amounts of it go into solution at the time of breaking up of monazite, it was not possible to add a fixed amount of TiO_2 to the 'blank' solution. However, a quick estimation of titanium could be made from the same sulphuric acid solution as the one used for uranium estimation and hence correction for the colour produced by titanium could be easily applied.

Since the 'blank' solution should contain approximately the same amounts of rare earths and phosphate as the sample solution it is necessary to know the percentage of these constituents in the samples to be analysed. This presents no serious difficulty with Indian monazite concentrates as the percentages of these constituents are fairly constant.

ACKNOWLEDGEMENT

The authors are indebted to Dr. Jagdish Shankar, for his guidance and for his keen interest and valuable suggestions during the course of this work.

Summary

Ammonium thiocyanate method can be used for the estimation of uranium in low grade ores after the preliminary isolation of uranium by ether extraction of the nitrate. A rapid method for the estimation of uranium in monazite concentrates is also described.

References

1. Bearse, A. E. and co-workers — *Chem. Eng. Progress*, 1954, **50**, 235.
2. Burstall, F. H. and Wells, R. A. — *Analyst*, 1951, **76**, 396.
3. Currah, J. E. and Beamish, F. E. — *Anal. Chem.*, 1947, **19**, 609.
4. Davenport, W. H. and Thomason, P. F. — *Ibid.*, 1949, **21**, 1093.
5. Harvey, C. O. .. *Bulletin of the Geological Survey of Great Britain, No* 3, His Majesty's Stationery Office, 1951, p. 50.
6. ———— .. *Ibid.*, p. 53.
7. Max Gerhold and Hecht, F. — *Mikrochem. Ver. Mikrochim. Acta.*, 1951, **36/37**, 1100.
8. Mellor .. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Co., London, 1946, **5**, 525.
9. Rodden, C. J. .. *Analytical Chemistry of the Manhattan Project*, McGrraw-Hill Book Co., New York, 1950, 104.
10. Sandell, E. B. .. *Colorimetric Determination of Traces of Metals*, Interscience Publishers, New York, 1944, pp. 433–38.
11. Wadia, D. N. .. *Geology of India*, Macmillan and Co., London, 1953, p. 480.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

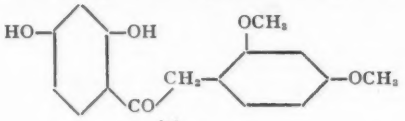
Part LV. A Synthesis of 7 : 7′–Dihydroxy Chromeno–(3′ : 4′ : 2: 3)–Chromone

By J. M. Sehgal and T. R. Seshadri, F.A.Sc.

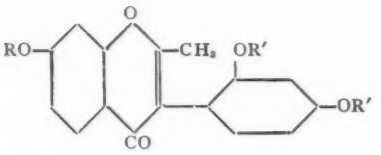
(Department of Chemistry, University of Delhi, Delhi-8)

Received July 8, 1955

In an earlier publication[1] the considerations that led to the discovery of a new route for the synthesis of chromenochromones were discussed and a simple member of the class, *i.e.*, 7-hydroxy chromeno-(3′ : 4′ : 2 : 3)-chromone was prepared. In developing this method for the synthesis of more complex types ultimately leading to the synthesis of the rotenoids themselves, a higher member of the series has now been prepared, *i.e.*, 7 : 7′-dihydroxy compound (V) starting from 2 : 4-dihydroxy phenyl 2′ : 4′-dimethoxy benzyl ketone (I). The various stages are represented by the following formulæ:

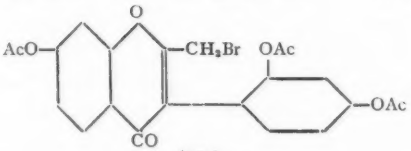


(I)

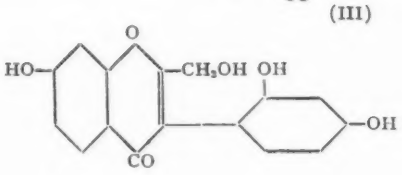


(II)

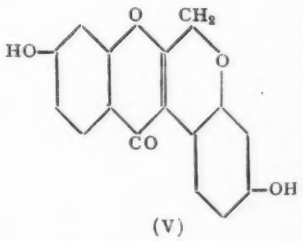
(*a*) R = Ac, R′ = Me (*b*) R = H, R′ = Me (*c*) R = R′ = H



(III)



(IV)



(V)

Experimental

2: 4-*Dimethoxyphenyl acetonitrile*

Method I.—The following improvements were made in the method of Mitter and Maitra.[2]

β-Resorcylaldehyde was methylated by the dimethyl sulphate and potassium carbonate method (40 hours) giving an improved yield of the dimethyl ether. Its conversion into the azlactone is more complete if the initial refluxing with hippuric acid and acetic anhydride for an hour is followed up by further heating for two hours on a boiling water-bath. A good yield of almost pure product is obtained by adding more alcohol and leaving the mixture overnight. When recrystallised it melted at 181–82° with slight sintering at 168°. Mitter and Maitra[2] reported it to melt at 168°. The pyruvic acid obtained by the decomposition of the azlactone melted at 161–62°. Mitter and Maitra, 156°. Its oxime could be crystallised from methanol as colourless needles melting at 148–49° (decomp.); Mitter and Maitra, 145°.

Method II.—2: 4-Dimethoxyphenyl acetic acid was prepared from resacetophenone dimethyl ether (27 g.) following the method of King and Neill[3] using Willgerodt reaction. It was found advantageous to remove excess of morpholine from the crude morpholide by distillation. The acetic acid (12 g.) was converted into the acid chloride by means of thionyl chloride and treated with ice-cold liquor ammonia (50 c.c.; 0·9) gradually in the course of 15–20 minutes. The solid amide was crystallised from hot water yielding colourless broad plates, m.p. 133–34°; 10 g. It (5 g.) was mixed with phosphorus pentoxide (8 g.) and distilled under reduced pressure when the nitrile passed over between 165–70° (5 mm.); m.p. 75–6° ; 2·2 g. The dehydration of the amide by refluxing with excess of acetic anhydride and sodium acetate for half an hour and subsequent treatment with ice did not give good yields.

2: 4-*Dihydroxyphenyl*-2′: 4′-*dimethoxy benzyl ketone* (*I*)

To a solution of 2: 4-dimethoxyphenyl acetonitrile (5 g.) and dry resorcinol (5 g.) in dry ether (150 c.c.) was added fused zinc chloride (2 g.) and the mixture saturated with dry hydrogen chloride (10 hours; 0° C.). The contents were left in an ice-chest for 24 hours when the ketimine hydrochloride first formed as a viscous liquid gradually solidified. It was separated, washed twice with small quantities of ether (20 c.c. each) and then heated with water (100 c.c.) in a boiling water-bath (6 hours). On cooling the ketone separated out. It was filtered and crystallized from dilute alcohol yielding colour-

less tiny prisms melting at 158–59°; 4·5 g. (Found: C, 66·8; H, 5·6; $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%). It gave a reddish pink colour with alcoholic ferric chloride.

7-Acetoxy-2′: 4′-dimethoxy-2-methyl isoflavone (II a)

The above dihydroxy ketone (I) (3 g.) was refluxed with acetic anhydride (25 c.c.) and fused sodium acetate (6 g.) in an oil-bath for 18 hours at 170–75° and then poured over crushed ice (500 g.) and stirred for 2 hours. The acetic acid formed was neutralized by aqueous sodium bicarbonate and the mixture left overnight in the refrigerator when the isoflavone (II *a*) separated as a crisp solid. It was crystallized from dilute alcohol and then from benzene-light petroleum mixture yielding colourless tiny prisms, m.p. 190–91°; 2·5 g. (Found: C, 67·3; H, 4·9; $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%).

7-Hydroxy-2′: 4′-dimethoxy-2-methyl isoflavone (II b)

The above acetoxy compound (II *a*) (0·2 g.) was refluxed with boiling alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.) for 2 hours, diluted with water (50 c.c.), and left in the refrigerator for 4 hours. The solid crystallized from ethyl acetate-petroleum ether mixture as grey coloured needles and rectangular prisms melting at 261–62°; 0·16 g. (Found: C, 68·6; H, 5·1; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%). 7: 2′: 4′-Trimethoxy-2-methyl isoflavone obtained by the methylation of the hydroxy compound (0·15 g.) with dimethyl sulphate and potassium carbonate in acetone medium crystallized from ethyl acetate-petroleum ether mixture as short prisms melting at 192–94°. Yield 0·15 g.

7: 2′: 4′-Trihydroxy-2-methyl isoflavone (II c)

(*a*) *With aluminium chloride.*—2-Methyl-7-acetoxy-2′: 4′-dimethoxy isoflavone (II *a*) (2·5 g.) was dissolved in dry benzene (100 c.c.), anhydrous aluminium chloride (7 g.) added and the mixture refluxed for 2 hours on a water-bath. The dark viscous mass left behind after removal of the solvent was treated with crushed ice (100 g.) and hydrochloric acid (25 c.c.). The mixture was boiled for 2 minutes and then cooled when the product solidified. It was dissolved in 2% cold aqueous sodium hydroxide (200 c.c.). The solution was extracted with ether and then acidified with hydrochloric acid when 7: 2′: 4′-trihydroxy-2-methyl isoflavone (II *c*) precipitated out. It crystallized from ethyl acetate and acetone mixture as colourless tiny prisms melting at 254–55° (decomp.); 1·1 g. (Found: C, 64·0; H, 4·7; $C_{16}H_{12}O_5$, H_2O requires C, 63·6; H, 4·6%). The compound did not give

any colour with alcoholic ferric chloride and also showed no fluorescence with concentrated sulphuric acid.

(*b*) *With hydriodic acid.*—2-Methyl-7-acetoxy-2′: 4′-dimethoxy isoflavone (II *a*) (0·5 g.) was heated with acetic anhydride (5 c.c.) and hydriodic acid (5 c.c.; d. 1·7) at 140–42° for 2 hours, then diluted with water (100 c.c.) and left in the refrigerator for 2 hours. The free iodine was removed by passing sulphur dioxide. The solid was filtered and crystallized from ethyl acetate-petroleum ether mixture; colourless prisms, m.p. 254–56° (decomp.); 0·1 g. 7: 2′: 4′-Triacetoxy-2-methyl isoflavone obtained by acetylation of the trihydroxy compound (0·4 g.) with acetic anhydride and sodium acetate crystallized from alcohol and then from carbon tetrachloride as short thick wedge-shaped prisms melting at 178–80°; 0·38 g. (Found: C, 63·9; H, 4·8; $C_{22}H_{18}O_8$ requires C, 64·4; H, 4·4%).

7: 2′: 4′-*Triacetoxy-2-bromomethyl isoflavone* (*III*)

A solution of the above triacetoxy isoflavone (0·62 g.), N-bromosuccinimide (0·27 g., 1 mole) and benzoyl peroxide (0·03 g.) in dry carbon tetrachloride (100 c.c.) was refluxed for 20 hours on a water-bath. The solvent was distilled off and the reddish yellow viscous mass left behind, washed with a large excess of boiling water (200 c.c., 2 lots) to remove succinimide and then treated with ice-cold water when a crisp solid was obtained. It crystallized from excess of alcohol as colourless needles melting at 201–03°; 0·45 g. (Found: C, 53·4; H, 3·7; $C_{22}H_{17}O_8Br$ requires C, 54·0; H, 3·5%).

7: 7′-*Dihydroxy-chromeno*-(3′: 4′: 2: 3)-*chromone* (*V*)

The above bromomethyl isoflavone (III) (0·4 g.) was refluxed with alcohol (20 c.c.) and hydrobromic acid (20 c.c., 40%) for 2 hours on a water-bath, diluted with water (100 c.c.) and left overnight in the refrigerator. 7: 2′: 4′-Trihydroxy-2-hydroxymethyl isoflavone (IV) that separated was collected and dried; 0·2 g. It did not give any test for bromine. Attempts to crystallize it were not successful and hence it was used as such for the next stage. It (0·2 g.) was dissolved in dry acetone (50 c.c.), ignited potassium carbonate (5 g.) added and the mixture refluxed for 12 hours, the solvent distilled off and the residue treated with ice-water (150 c.c.), when a clear solution was obtained which on acidification yielded the chromeno-chromone (V). It crystallized from alcohol as short prisms, m.p., 280–82° (sinters at 266°) 0·08 g. (Found: C, 64·3; H, 4.4; $C_{16}H_{10}O_5$, H_2O requires C, 64·0; H, 4.0%).

SUMMARY

Using N-bromosuccinimide, a synthesis of 7: 7′-dihydroxychromeno-(3:′ 4′: 2: 3) chromone has been effected. 7: 2′: 4′-Triacetoxy-2-methyl isoflavone is brominated to give the 2-bromomethyl isoflavone which is cyclized, after hydrolysis, to the corresponding chromenochromone.

REFERENCES

1. Seshadri and Varadarajan *Proc. Ind. Acad. Sci.*, 1953, **37 A**, 784.
2. Mitter and Maitra .. *Jour. Ind. Chem., Soc.*, 1936, **13**, 236.
3. King and Neill .. *Jour. Chem. Soc.*, 1952, 4752.

A NOTE ON INGHAM SUMMABILITY AND SUMMABILITY BY LAMBERT SERIES

By C. T. Rajagopal

(Ramanujan Institute of Mathematics, Madras)

Received June 22, 1955

(Communicated by Professor B. S. Madhava Rao, F.A.SC.)

1. Introduction

Let $\sum_1^\infty a_n$ be a given series and let λ denote the sequence $\{\lambda_n\}$ which is such that

$$0 < \lambda_1 < \lambda_2 < \lambda_3 < \cdots, \ \lambda_n \to \infty. \tag{1}$$

Then the transform of $\sum_1^\infty a_n$, defined by the series

$$\Phi_\lambda(t) = \sum_1^\infty a_n \phi(\lambda_n t), \ t > 0, \tag{2}$$

supposed to be convergent, is regular provided that, for $u \geqslant 0$,

$$\phi(u) = \int_0^\infty \psi(x)\, dx \ \text{ where } \psi(x) \geqslant 0, \ \phi(0) = 1. \tag{3}$$

In these circumstances, whenever $\Phi_\lambda(t) \to s$ as $t \to +0$, we may say that Σa_n is summable to s by the regular method (Φ, λ) and refer to $\Phi_\lambda(t)$ as the (Φ, λ)-transform of Σa_n. I have obtained elsewhere[7–11] a variety of theorems connecting the (Φ, λ)-transform of Σa_n with the partial sums of Σa_n, assuming that the function $\psi(x)$ defined in (3) satisfies some or all of the conditions:

$$\left.\begin{array}{l} \psi(u) \text{ is positive monotonic-decreasing in } (0, \infty), \\ \int_0^\infty \psi(u)\, du = 1, \ \int_0^\infty \psi(u) |\log u|\, du < \infty, \ \int_0^\infty \psi(u) u^{ix} du \neq 0 \ (-\infty < x < \infty).^* \end{array}\right\} \tag{C}$$

* In the applications which concern us here $\psi(u)$ satisfies (C) in a slightly more restricted form given elsewhere ([7] p. 377). On the other hand, in applications of another kind ([8] Theorems 2 a, 2 b, 1, 2, [9, 10]) the conditions (C) may be relaxed.

My theorems include applications to the two cases

$$\phi(u) = e^{-u}, \tag{4 a}$$

$$\phi(u) = u/(e^u - 1) \text{ for } u > 0, \ \phi(0) = 1, \tag{4 b}$$

which give rise to the methods of summability (A, λ), (L, λ)† respectively associated with the names of Abel and Lambert.

Connected with the method (A, λ), there is the Riesz method (R, λ, κ), $\kappa \geqslant 0$, in which the transform of Σa_n is given by

$$C_\kappa(x) \equiv \frac{A_\kappa(x)}{x^\kappa} = \begin{cases} \dfrac{\kappa}{x^\kappa} \int_0^x A(u)(x-u)^{\kappa-1}\, du \text{ for } \kappa > 0, \\ A(x) \text{ for } \kappa = 0, \end{cases} \tag{5}$$

where $A(x)$ is defined, with reference to the $\{\lambda_n\}$ in (1):

$$A(x) = \sum_{\lambda_n < x} a_n \text{ for } x > \lambda_1, \ A(x) = 0 \text{ for } x \leqslant \lambda_1. \tag{6}$$

And summability to s by the method (R, λ, κ), or summability—(R, λ, κ) is defined: $\lim C_\kappa(x) = s$ as $x \to \infty$. Pennington[4] has shown that, connected with the method (L, λ), in the same way as the method (R, λ, κ) is with the method (A, λ), there is the method (I, λ, κ), $\kappa \geqslant 0$, originating with Ingham, in which the transform of Σa_n is defined:

$$S_\kappa(x) \equiv \frac{(\kappa+1)\, T_\kappa(x)}{x^{\kappa+1}} = \begin{cases} \sum_{\lambda_n < x} a_n \chi_\kappa(\lambda_n / x) \text{ for } x > 0, \\ 0 \text{ for } x = 0. \end{cases} \tag{7}$$

where $\{\lambda_n\}$ is the sequence in (1) and

$$\chi_\kappa(u) = (\kappa+1)\, u \sum_{r < 1/u} (1 - ru)^\kappa, \ u > 0.$$

And summability to s by the method (I, λ, κ) or summability—(I, λ, κ) is defined: $\lim S_\kappa(x) = s$ as $x \to \infty$.‡

† Ganapathy Iyer[1] has studied a generalization of the method (L, λ) in which the $\phi(u)$ of (4 b) is replaced by

$$\phi(u) = \frac{\alpha u}{e^u - e^{(1-\alpha)u}}, \ \alpha > 0, \text{ for } u > 0, \ \phi(0) = 1. \tag{4' b}$$

‡ (I, λ, 0)-summability, in the case $\lambda_n = n$, reduces to Ingham's (I)-summability defined in Hardy [[2] Appendix IV].

This note supplements Pennington's discussion by (i) stating theorems which bring out some aspects of the connexion between (L, λ)-summability and (I, λ, κ)-summability, exactly analogous to certain known aspects of the connexion between (A, λ)-summability and (R, λ, κ)-summability, (ii) touching on aspects of the connexion between (L, λ)-summability, or more generally (Φ, λ)-summability, and (R, λ, κ)-summability, analogous to those of the connexion between (L, λ)-summability and (I, λ, κ)-summability. An appendix gives an unpublished example of T. Vijayaraghavan's, simpler than one of Pennington's, to show that the method of summability (I, λ, 0) is not regular.

2. Theorems Connecting the Methods (L, λ) and (I, λ, κ)

Three of these theorems are stated here without proof. Because they can be proved exactly like the analogous theorems connecting (A, λ)-summability with (R, λ, κ)-summability which either I[5] or Jakimovski and I[3] have proved, in virtue of Pennington's lemmas [[4] Lemmas 1, 2] stated below whose purport is that, in the following well-known formulae, we can replace $A_{\kappa+1}(x)$ defined as in (5) by $(\kappa+1)\,T_\kappa(x)$ defined as in (7), and the (A, λ)-transform of Σa_n by the (L, λ)-transform.

$$A_{\kappa+\rho+1}(x) = \frac{\Gamma(\kappa+\rho+2)}{\Gamma(\kappa+2)\,\Gamma(\rho)} \int_0^x A_{\kappa+1}(u)\,(x-u)^{\rho-1}du, \quad \kappa+1 \geqslant 0,\ \rho > 0$$

[[2] p. 111, (5. 14. 3)].

$$\sum_1^\infty a_n e^{-\lambda_n t} = \frac{t^{\kappa+2}}{\Gamma(\kappa+2)} \int_0^\infty A_{\kappa+1}(u)\,e^{-tu}\,du, \quad \kappa+1 \geqslant 0, \tag{8}$$

whenever the series is convergent (for $t > 0$) [[2] p. 136, (6. 8. 6)].

Lemma 1.—*If* $\kappa \geqslant 0$, $\rho > 0$, *and* $T_r(x)$, $r \geqslant 0$, *is defined as in* (5), *then*

$$T_{\kappa+\rho}(x) = \frac{\Gamma(\kappa+\rho+1)}{\Gamma(\kappa+1)\,\Gamma(\rho)} \int_0^x T_\kappa(u)\,(x-u)^{\rho-1}\,du \quad (x \geqslant 0).$$

Lemma 2.—*If* $\kappa \geqslant 0$, *and* $T_\kappa(x)$ *is defined by* (5), *then*

$$L_\lambda(t) = \sum_1^\infty a_n \frac{\lambda_n t}{e^{\lambda_n t} - 1} = \frac{t^{\kappa+2}}{\Gamma(\kappa+1)} \int_0^\infty T_\kappa(u)\,e^{-tu}\,du \quad (t > 0) \tag{9}$$

provided that the series is convergent. In the case in which the series is absolutely convergent, the integral is likewise so.

The statement in Lemma 2 that the absolute convergence of the integral there follows from that of the series does not appear in Pennington [4 Lemma 2] but is obvious from the proof in Pennington, *loc. cit.*

THEOREM I.—*Let* $L_\lambda(t)$ *be defined as in* (9) *and* $S_r(x)$, $r \geqslant 0$, *as in* (7). *Let*

$$\overline{\lim_{x\to\infty}}\, S_\kappa(x) = \bar{S}_\kappa, \quad \underline{\lim_{x\to\infty}}\, S_\kappa(x) = \underline{S}_\kappa,$$

$$\lim_{\kappa\to\infty} \bar{S}_\kappa = \bar{S}_\infty, \qquad \lim_{\kappa\to\infty} \underline{S}_\kappa = \underline{S}_\infty,$$

where the last two limits exist on account of $\bar{S}_\kappa$ *and* $\underline{S}_\kappa$ *being monotonic functions of* κ, *the first decreasing and the second increasing* [4 Theorem 1]. *Then*

(*a*) $\overline{\lim_{t\to+0}}\, L_\lambda(t) = \bar{S}_\infty$ *provided that* $\bar{S}_\infty > -\infty$,

(*b*) $\underline{\lim_{t\to+0}}\, L_\lambda(t) = \underline{S}_\infty$ *provided that* $\bar{S}_\infty < \infty$,

(*c*) $\overline{\lim_{t\to+0}}\, L_\lambda(t) = \bar{S}_\infty$, $\underline{\lim_{t\to+0}}\, L_\lambda(t) = \underline{S}_\infty$ *provided that*

$$-\infty < \underline{S}_\infty < \infty.$$

THEOREM II.—*Let* $\mathcal{L}(x)$ *be a positive and continuous function of* $x > 0$ *such that* $\mathcal{L}(ux) \sim \mathcal{L}(x)$, $u > 0$, $x \to \infty$. *Let* $L_\lambda(t)$ *be defined as in* (9) *and* $S_r(x)$, $T_r(x)$, $r \geqslant 0$, *as in* (7). *Then the two conditions*

$$L_\lambda(t) \sim s\mathcal{L}(t^{-1}) \quad (t \to +0),$$

either
$$\lim_{1<\lambda\to1} \underline{\lim_{x\to\infty}}\ \operatorname{bound}_{x<y<\lambda x} \left[\frac{T_{k\kappa}(y) - T_\kappa(x)}{x^{\kappa+1}\,\mathcal{L}(x)}\right]$$

or
$$\lim_{1<\lambda\to1} \underline{\lim_{x\to\infty}}\ \operatorname{bound}_{x<y<\lambda x} \left[\frac{S_{k\kappa}(y)}{\mathcal{L}(y)} - \frac{S_\kappa(x)}{\mathcal{L}(x)}\right]$$

$\Bigg\}\geqslant 0, \qquad k \geqslant 0,$

together imply that

$$S_\kappa(x) \sim s\,\mathcal{L}(x) \quad (x \to \infty).$$

THEOREM III.—*Let* $L_\lambda(t)$ *be defined as an absolutely convergent series*§ *by* (9) *and* $S_r(x)$, $r \geqslant 0$, *as in* (7). *Then the two conditions*

§ In the analogue of Theorem III for summabilities (A, λ) and (R, λ, κ), we assume only the convergence of $\sum a_n e^{-\lambda_n t}$, this being enough to secure the absolute convergence of the integral in (8). In Theorem III, on the other hand, we secure the absolute convergence of the integral by means of that of the series $L_\lambda(t)$.

$$L_\lambda(t) \to s \quad (t \to +0), \tag{10}$$

$$S_\kappa(x) - S_{\kappa+1}(x) = O_L(1), \ \kappa \geqslant 0 \quad (x \to \infty), \tag{11}$$

together ensure that

$$S_{\kappa+1}(x) \to s \quad (x \to \infty). \tag{12}$$

COROLLARY III. 1. *Theorem III may be restated with* (11) *alone changed to*

$$S_\kappa(x) = O_L(1), \ \kappa \geqslant 0 \quad (x \to \infty). \tag{11'}$$

For (11') and (10) together can be shown to imply that $S_{\kappa+1}(x) = O_R(1)$ and so to imply (11).

COROLLARY III. 2. *If, in Theorem III,* $O_L(1)$ *is changed to* $O(1)$ *in condition* (11), *conclusion* (12) *will assume the stronger form that, for every* $\epsilon > 0$,

$$S_{\kappa+\epsilon}(x) \to s.$$

All the preceding results have precise analogues, for the methods (A, λ) and (R, λ, κ), proved elsewhere [[5] Theorem 2, [3] Theorem I', [5] Theorem 1 or [3] Corollary II'.2, [3] Corollary III'.1]. On account of Lemmas 1, 2, they can, in fact, be deduced from the proofs of their analogues by replacing the (A, λ)-transform of Σa_n in the proofs by the (L, λ)-transform and

$$C_{r+1}(x) \equiv \frac{A_{r+1}(x)}{x^{r+1}}, \ r+1 \geqslant 0, \text{ by } S_r(x) \equiv \frac{(r+1)\ T_r(x)}{x^{r+1}} \ r \geqslant 0.$$

Theorem I which is Abelian in character supplements Pennington's result [[4] Theorem 2] connecting the oscillation of $L_\lambda(t)$ as $t \to +0$ with that of $S_\kappa(x)$ as $x \to \infty$; while Theorems II, III are Tauberian counterparts of the consequence, of the same result of Pennington's, that the convergence of $L_\lambda(t)$ (to s) is implied by that of $S_\kappa(x)$ (to s).

3. THEOREMS CONNECTING THE METHODS (Φ, λ) AND (R, λ, κ)

In connexion with the last clause of the last sentence, it is worthwhile noticing a parallel result, namely, that *the convergence of* $L_\lambda(t)$ *to* s, *or more generally that of* $\Phi_\lambda(t)$ *as defined by* (1) *to* s, *is implied by the convergence of* $C_\kappa(x)$ *as defined by* (5) *to* s, *in the cases of the* $\phi(u)$ *of* (4 *a*) *and* (4 *b*)** *as well as in the case of*

$$\phi(u) = 1/(1+u)^\rho, \ \rho > 0, \tag{4 c}$$

** *Cf.* Hardy [[3] Appendix IV, Theorem 259].

which gives a summability method (Φ, λ) associated with the name of Stieltjes. In all these cases $\phi(u)$ satisfies the conditions:

$$\left.\begin{aligned} &\psi(u) = -\phi'(u) \text{ has derivatives of all orders } k, \\ &(-1)^k \psi^{(k)}(u) \geqslant 0 \text{ for all large } u. \end{aligned}\right\} \tag{D}$$

The last-mentioned result is formally enunciated as the next theorem and its proof depends on the following lemma which I have proved elsewhere [6 Lemma 2].

LEMMA 3.—*If $A(u)$ is any function, of bounded variation in every finite interval of $(0, \infty)$ and such that $A(0) = 0$ and if $\phi(u)$, defined in $(0, \infty)$ as an integral, is positive and ultimately monotonic decreasing, then*

$$\int_0^\infty \phi(ut)\, d\{A(u)\} = t \int_0^\infty \psi(ut)\, A(u)\, du \ (t > 0), \text{ where } \phi(u) = \int_u^\infty \psi(x)\, dx,$$

in every case in which the first integral is convergent.

THEOREM IV.—*Let the (Φ, λ)-transform of $\sum_1^\infty a_n$ be defined as the series $\Phi_\lambda(t)$ of (2) for $t > 0$, $\phi(u)$ being defined in terms of $\psi(u)$ as in (3) and $\psi(u)$ satisfying conditions (D). Also, let $C_\kappa(x)$, $A_\kappa(x)$ $\kappa \geqslant 0$, be defined by (5) for $x \geqslant 0$. Then*

$$\lim_{x \to \infty} C_\kappa(x) = \lim_{x \to \infty} \frac{A_\kappa(x)}{x^\kappa} = s, \tag{13}$$

for any $\kappa \geqslant 0$ implies that

$$\lim_{t \to +0} \Phi_\lambda(t) = s.$$

Proof.—The case $\kappa = 0$ is trivial [*e.g.*, 4 Theorem 5], even the convergence of $\Phi_\lambda(t)$, $t > 0$, following from that of Σa_n or $A(x)$. In any case we may suppose without loss of generality that κ is an integer, if not 0, and get, by $\kappa+1$ successive applications of Lemma 3†† all justified by (D),

$$\begin{aligned} \Phi_\lambda(t) &= \int_0^\infty \phi(ut)\, d\{A(u)\} \\ &= t \int_0^\infty \psi(ut)\, A(u)\, du = t^2 \int_0^\infty -\psi'(ut)\, A_1(u)\, du = \cdots \\ &= \frac{t^{\kappa+1}}{\Gamma(\kappa+1)} \int_0^\infty (-1)^\kappa \psi^{(\kappa)}(ut)\, A_\kappa(u)\, du. \end{aligned} \tag{15}$$

†† Since we use only Lemma 3 in our proof, we may relax the condition in (3) that $\psi(x) > 0$ to the condition that $\psi(x) \geqslant 0$ ultimately or that $\phi(x)$ is ultimately monotonic decreasing. Theorem IV with this relaxation applies also to Ganapathy Iyer's kernel $\phi(u)$ in (4′ *b*) of the first footnote [*e.g.*, 1 converse part of Theorem (1)].

Hence, replacing $A(u)$ by $A(u) - s$ in the last two lines, we get

$$\Phi_\lambda(t) - s = t\int_0^\infty \psi(ut)\{A(u) - s\}\,du$$

$$= \frac{t^{\kappa+1}}{\Gamma(\kappa+1)}\int_0^\infty (-1)^\kappa \psi^{(\kappa)}(ut)\{A_\kappa(u) - su^\kappa\}\,du. \tag{16}$$

On account of (13) we can find positive constants U and K, corresponding to $\epsilon > 0$, so that

$$|A_\kappa(u) - su^\kappa| < \begin{cases} \epsilon u^\kappa \text{ for } u > U, \\ Ku^\kappa \text{ for } u \leqq U. \end{cases}$$

Therefore we obtain from (16)

$$|\Phi_\lambda(t) - s| < \frac{K}{\Gamma(\kappa+1)}\int_0^{Ut} |(-1)^\kappa \psi^{(\kappa)}(u)|\,u^\kappa\,du$$

$$+ \frac{\epsilon}{\Gamma(\kappa+1)}\int_{Ut}^\infty |(-1)^\kappa \psi^{(\kappa)}(u)|\,u^\kappa du.$$

This leads at once to (16) when $t \to +0$ since $\int_0^\infty |(-1)^\kappa \psi^{(\kappa)}(u)|\,u^\kappa\,du < \infty$ as a result of (D) and the following relation obtained by putting $A(u) \equiv 0$, $s = -1$ in (16):

$$t\int_0^\infty \psi(ut)\,du = \frac{t^{\kappa+1}}{\Gamma(\kappa+1)}\int_0^\infty (-1)^\kappa \psi^{(\kappa)}(ut)\,u^\kappa\,du,$$

$$\text{or } 1 = \frac{1}{\Gamma(\kappa+1)}\int_0^\infty (-1)^\kappa \psi^{(\kappa)}(u)\,u^\kappa\,du.$$

Reference may be made here to Tuaberian theorems elsewhere [11 Theorem $\bar{\text{A}}$, $\bar{\text{B}}$]‡‡ which are conditional converses of Theorem IV on the hypothesis that $\psi(u)$ is subject to (C) in its entirety or otherwise, and which are, in fact, analogues of Theorem III and its corollaries with $\Phi_\lambda(t)$ and $C_\tau(x)$ instead of $L_\lambda(t)$ and $S_\tau(x)$ respectively.

‡‡ In these theorems, carried over from Theorems A, B, [11] there is the hypothesis that $\psi(x)$ is an integral which is superfluous.

APPENDIX

Pennington [4 Theorems, 3, 4] has shown that the method of summability (I, λ, κ), though regular for $\kappa > 0$, is not so for $\kappa = 0$, constructing a series Σa_n which is convergent but not summable-(I, λ, 0) in consequence of the fact (4 p. 73):

$$\overline{\lim_{\substack{n\to\infty \\ n \text{ odd}}}} \frac{\sum_{d/n} d}{n \log\log n} = \tfrac{1}{2}e^{\gamma}.$$

The late Dr. T. Vijayaraghavan supplied me with the following series which serves the same purpose and has the advantage that it can be handled without any special tool.

Let $\sum_1^\infty a_n$ *be defined with reference to a sequence*

$$\mu_r = \nu_r! \text{ where } \nu_r = 3^{r^2},\ r = 1, 2, 3\ldots. \tag{17}$$

$$a_n = \left\{ \begin{array}{l} \left\{ \begin{array}{l} \frac{1}{r} \text{ if } n = \frac{\mu_r}{t}, \\ -\frac{1}{r} \text{ if } n = \frac{\mu_r}{t} - 1, \end{array} \right\} t = 1, 2, \ldots, \nu_r, \quad r \geqslant 2, \\ a_n = 0 \text{ otherwise.} \end{array} \right\} \tag{18}$$

Then Σa contains successive groups of $2\nu_2, 2\nu_3, \ldots$ non-zero terms each of which has some zero terms as well and is situated between two groups of only zero terms. For every $r \geqslant 2$, we shall call the group containing $2\nu_r$ non-zero terms the rth group, ignoring (as is permissible in the computations which follow) the other groups of only zero terms. *It is trivial that* Σa_n *converges to* 0, *while it can be easily proved that* Σa_n *is not* (I, λ, 0)*-summable in the case in which* λ *is the sequence of positive integers* $\{n\}$.

When λ is the sequence $\{n\}$ and Σa_n is any given series, the definition (7) of $S_\kappa(x)$ makes

$$S_0(x) = \sum_{n<x} a_n \chi_0(n/x)$$

where

$$\chi_0(u) = u \sum_{r<1/u} 1 = \begin{cases} 1 - u \text{ if } 1/u \text{ is an integer,} \\ u\,\mathrm{I}(1/u) \text{ if } 1/u \text{ is not an integer,} \end{cases} \tag{19}$$

$\mathrm{I}(x)$ denoting the integral part of x. It will be proved now that, for the series Σa_n defined above,

$$\lim_{r\to\infty} S_0(u_r) = -\infty, \textit{ i.e., } \underline{\lim_{x\to\infty}}\, S_0(x) = -\infty.$$

In the first place, the contribution to $S_0(\mu_r)$ of the rth group arises from values of n such that $(\mu_r/\nu_r) - 1 \leqslant n < \mu_r$; and, in consequence of (18) and (19),

$$\chi_0\left(\frac{n}{\mu_r}\right) = \begin{cases} 1 - \dfrac{n}{\mu_r} \text{ if } \dfrac{\mu_r}{n} = t,\ t = 2, 3, \dots, \nu_r, \\ \dfrac{n}{\mu_r} \mathrm{I}\left(\dfrac{\mu_r}{n}\right) \text{ if } \dfrac{\mu_r}{n} = t + \dfrac{t}{n},\ t = 1, 2, \dots, \nu_r, \end{cases}$$

where $\mathrm{I}(\mu_r/n) = \mathrm{I}(t + t/n) = t$ since t/n in the second case is less than $\nu_r/[(\mu_r/\nu_r) - 1]$ which is a proper fraction by definition (17) of ν_r. Therefore

$$\sum_{(\mu_r/\nu_r)-1 \leqslant n < \mu_r} a_n \chi_0\left(\frac{n}{\mu_r}\right) = \sum_{t=2}^{\nu_r} \frac{1}{r}\left(1 - \frac{1}{t}\right) - \sum_{t=1}^{\nu_r} \frac{1}{r}\left(\frac{1}{t} - \frac{1}{\mu_r}\right) t$$

$$= -\frac{1}{r} \sum_{t=1}^{\nu_r} \frac{1}{t} + \frac{1}{r\mu_r} \sum_{t=1}^{\nu_r} t$$

$$< -\frac{1}{r} \log(\nu_r + 1) + \frac{\nu_r(\nu_r + 1)}{2r\mu_r} \to -\infty \quad (20)$$

as $r \to \infty$ since, in virtue of our definition (17) of ν_r,

$$-\frac{1}{r}\log(\nu_r + 1) \sim -\frac{\log 3^{r^2}}{r} \to -\infty, \quad \frac{\nu_r(\nu_r + 1)}{2r\mu_r} \sim \frac{1}{2r(\nu_r - 2)!} \to 0.$$

We next estimate the contribution to $S_0(\mu_r)$ of the kth group, $2 \leqslant k \leqslant r - 1$, using the fact that, in both cases of (19), $1 - u \leqslant \chi_0(u) < 1$. As a result of this,

$$|\chi_0(u) - \chi_0(v)| < \max(u, v),$$

and the contribution to $S_0(\mu_r)$ from the two terms a_n of the kth group corresponding to $n = \mu_k/t$ and $n = (\mu_k/t) - 1$ has absolute value

$$\frac{1}{k}\left|\chi_0\left(\frac{\mu_k/t}{\mu_r}\right) - \chi_0\left(\frac{(\mu_k/t) - 1}{\mu_r}\right)\right| < \frac{\mu_k}{k\mu_r t} \leqslant \frac{\mu_k}{k\mu_r}.$$

This makes the contribution to $S_0(\mu_r)$ of the kth group less in absolute value than $\nu_k\mu_k/k\mu_r$ and gives us, when we take into account the cntribution of all the kth groups for which $2 \leqslant k \leqslant r - 1$,

$$\left|\sum_{1 \leqslant n < (\mu_r/\nu_r)-1} a_n \chi_0\left(\frac{n}{\mu_r}\right)\right| < \sum_{k=2}^{r-1} \frac{\nu_k\mu_k}{k\mu_r}.$$

By our definition (17) of ν_r and μ_r, the right-hand member of the above inequality tends to a finite limit as $r \to \infty$, and so this inequality taken in conjunction with (20) shows that $S(\mu_r) \to -\infty$ as $r \to \infty$.

REFERENCES

1. Ganapathy Iyer, V. .. "Tauberian theorems on generalised Lambert's series," *J. Ind. Math. Soc.* (New Series), 1934, **1**, 73–87.
2. Hardy, G. H. .. *Divergent Series* (Oxford, 1949).
3. Jakimovski, A. and Rajagopal, C. T. "Applications of a theorem of O. Szász for the product of Cesàro and Laplace transforms," *Proc. Amer. Math. Soc.*, 1954, **5**, 370–84.
4. Pennington, W. B. .. "On Ingham summability and summability by Lambert series," *Proc. Camb. Phil. Soc.*, 1955, **51**, 65–80.
5. Rajagopal, C. T. .. "On Riesz summability and summability by Dirichlet's series," *Amer. J. Math.*, 1947, **69**, 371–78, 851–52 and 1954, **76**, 252–58.
6. ———— .. "A note on 'positive' Tauberian theorems." *J. London Math. Soc.*, 1950, **25**, 315–27.
7. ———— .. "Note on some Tauberian theorems of O. Szász," *Pacific J. Math.*, 1952, **2**, 377–384.
8. ———— .. "A generalization of Tauber's theorem and some Tauberian constants," *Math. Z.*, 1953, **57**, 405–14 and 1954, **60**, 142–47.
9. ———— .. "On a absolute constant in the theory Tauberian series (II)," *Proc. Ind. Acad. Sci.*, 1954, **39 A**, 272–81.
10. ———— .. "On an one-sided Tauberian theorem: a further note," *J. Ind. Math. Soc.* (New Series), 1953, **17**, 33–42.
11. ———— .. "Theorems on the product of two summability methods with applications," *ibid.* (New Series), 1954, **18**, 89–105.

934-55 Printed at the Bangalore Press, Bangalore City, by C. Vasudeva Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably) twice the size than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of author; Name of Journal (abbreviation) with a single underline; Year of publication; Number of Volume with a double underline, and lastly page. The following would be a useful illustration:—

Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Authors will be supplied with reprints of their papers at cost price, if intimation is given at the time of returning the slip-proof.

Blocks appearing in the *Proceedings* will be available for purchase by their respective authors. Orders for the same should be sent along with the corrected proofs and in any case not later than one month after the date of publication of the paper. The price charged would be 25% of the actual cost of the blocks *plus* freight and despatching charges. If the blocks are reproduced in other journals or publications, due acknowledgment should be made in them to the *Proceedings*.

The original drawings and plates of blocks appearing in the *Proceedings* will be returned to such of the authors as may require them provided the cost of despatching such originals is borne by them.

CONTENTS

	PAGE
The Elastic Behaviour of Isotropic Solids . . . . . Sir C. V. Raman and K. S. Viswanathan	1
Thermal Expansion of Boric Acid . . . . . M. A. Lonappan	10
Analysis of τ-Mesons . . . . . P. S. Goel and K. A. Neelakantan	22
Colorimetric Estimation of Uranium with Ammonium Thiocyanate and its Application to Determination of Uranium in Minerals Particularly Monazite Concentrates . . . . . Mahadeo M. Tillu, D. V. Bhatnagar and T. K. S. Murthy	28
Synthetic Experiments in the Benzopyrone Series. Part LV. A Synthesis of 7 : 7′-Dihydroxy Chromeno-(3′ : 4′ : 2 : 3)-Chromone . . . . . J. M. Sehgal and T. R. Seshadri	36
A Note on Ingham Summability and Summability by Lambert Series . . . . . C. T. Rajagopal	41